Hollow Polyelectrolyte Shells: Exclusion of Polymers and Donnan Equilibrium

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Hollow polyelectrolyte capsules were fabricated by means of stepwise adsorption of polyelectrolytes followed by dissolution of the templating core. The capsule wall thickness was approximately 20 nm. The diameter of the capsules is given by the size of the templates (3.3 μm). These capsules exclude poly(styrenesulfonate) (PSS) from a molecular weight of 4200 upward but are permeable for small ions and 6-carboxyfluorescein (6-CF). By means of adding PSS in acidic form to the bulk solution, a Donnan equilibrium between the bulk and internal solution encapsulated within the capsules was created. The pH in the capsule interior is more basic. This difference in pH is larger than a unit for capsules of 3.3 μm in diameter. Addition of NaCl decreases this pH difference. A theoretical model is developed that describes the observed pH difference. The essential assumptions of the model are the selective permeability of the capsule wall, charging of the capsule together with its interior according to its capacitance, and an osmotic balance of the system. The developed shell system represents a novel class of stable colloids combining the compartmentalization of an aqueous solution with the possibility of creating pH differences on the micrometer scale.

Introduction

Supramolecular multicomponent nanostructures, such as ultrathin polymer films, surface-modified liposomes, and organic−inorganic composite nanosized materials, have recently met increasing interest in various fields of applied physical chemistry. At present, a variety of materials, such as a wide range of synthetic polyelectrolytes, biopolymers, lipids, and inorganic particles, have been successfully employed to fabricate multilayer films onto flat substrates by taking advantage of the electrostatic interaction between oppositely charged species during their stepwise adsorption from an aqueous solution.[1−8] Recently, this technology has been also applied for multilayer assembling on the surface of colloidal particles.[9−11] It has been further demonstrated that a novel type of hollow polyelectrolyte micro- and nanocapsules can be fabricated by means of dissolving the original templating core.[10] The compartmentalization of materials in the small capsule volumes with controlled thickness, composition, and permeability of the encapsulating wall opens perspectives for use of these structures as microreactors, microcarriers, and sustained drug release formulations.

According to the basic concept of the driving force of macroion multilayer assembly, the ζ potential of colloidal particles alternates between positive and negative values at each step of the polyelectrolyte adsorption. The film thickness grows linearly with the number of layers. The thickness increase was found to be approximately 2 nm/layer of adsorbed polyelectrotroyte.[11]

Figure 1 provides a scheme of the fabrication of hollow polyelectrolyte shells. After dissolution of the templating melamine formaldehyde core at low pH, the assembled polyelectrolyte films remain intact.[10] The capsule size and wall thickness are determined by the size of the original colloids and the number of adsorbed polyelectrolyte layers, respectively.

In principle, permeability features of the capsule wall, such as selectivity for water-soluble components, could be used to create a difference in the chemical composition between the bulk solution and the capsule interior. This is an intriguing situation concerning possible applications of the microcapsules as microreactors or microcarriers. However, at present little is known about the permeability properties of these free polyelectrolyte films. A convenient approach to study and to employ the selective permeability properties of the capsule walls is to create a Donnan equilibrium situation. For example, if an electrolyte species is excluded from the encapsulated interior, the permeant counterions should be distributed on both sides of the shell wall according to the Donnan equilibrium. Hence, their concentration should be different on both sides of the capsule wall. In the case of protons this would correspond to a pH difference. Furthermore, the presence of a nonpermeating electrolyte species in the solution on one side of the capsule wall can induce an osmotic pressure difference across the wall. This may eventually lead to volume changes of the hollow polyelectrolyte capsules and can reflect mechanical properties of the shell wall.

Thus, the aim of this work focuses on the experimental demonstration of this situation. A theoretical consideration of the distribution of small ions taking into account the Donnan equilibrium together with the osmotic response of the capsules is also provided.

Experimental Details

Materials. Sodium poly(styrenesulfonate) (Na-PSS, MW $\sim$ 70 000) and poly(allylamine hydrochloride) (PAH, MW $\sim$ 50 000) were obtained from Aldrich. All commercial polyelectrolytes were used without further purification except for PSS, which was dialyzed against Milli-Q water (MW cutoff 14 000) and lyophilized. For confocal fluorescence microscopy the PAH

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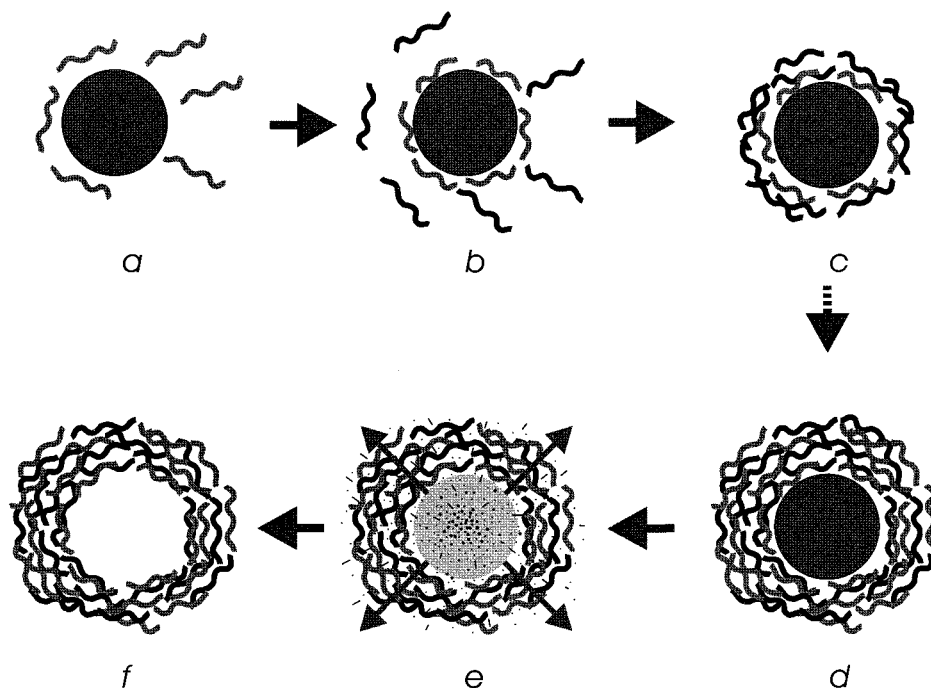*J. Phys. Chem. B, Vol. 103, No. 31, 1999* **6435**

Figure 1. Scheme demonstrating the consecutive adsorption of positively (gray) and negatively (black) charged polyelectrolytes onto negatively charged colloidal particles (a−d). After (e) the colloidal core was dissolved (e), a suspension of hollow polyelectrolyte capsules is obtained (f).
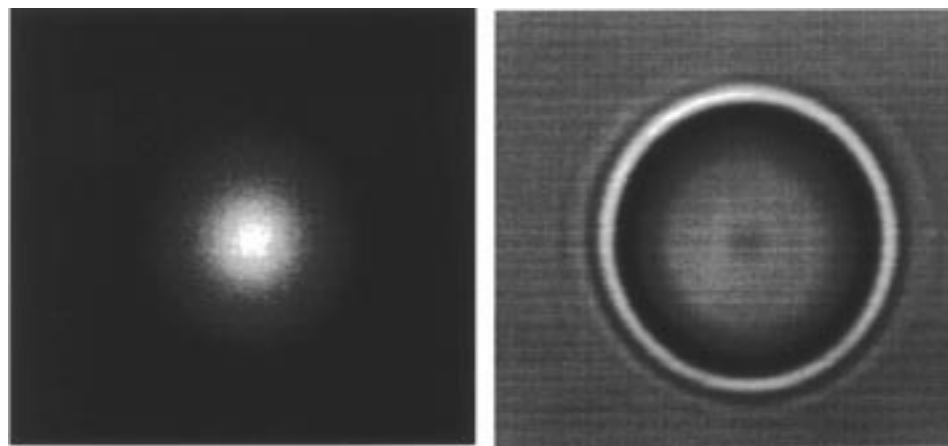

Figure 2. Confocal microscopy image (left) of a polyelectrolyte capsule containing as fluorescent marker 6-CF covalently bound to melamin formaldehyde. The right image provides the standard microscopic image taken in parallel.

was labeled with fluorescein isothiocyanate (PAH−FITC).[11]

Suspensions of monodisperse melamine formaldehyde particles (MF particles) with 3 μm diameter were purchased from Microparticles GmbH. These particles dissolve at pH values less than 1.6 and have been used as templates for the production of hollow polyelectrolyte capsules.[9,10] To monitor the pH value inside the hollow poylectrolyte shells the MF particles have been labeled with fluorescein isothiocyanate and partially cross-linked. Some labeled rest of the MF particles was not released across the shell walls and was used below as a pH-sensitive probe (Figure 2).

Na-PSS of molecular weights of 4200, 13 600, 32 200, and 70 000 was purchased from Polymer Standards Service (Darmstadt, Germany). The solutions of Na-PSS were dialyzed against Milli-Q water until the conductivity of the outer solution reached 1 μS/cm. Then Na$^+$ was exchanged with H$^+$ by passing it through a cation exchange column filled with Dowex Monosphere 650C (Sigma). This stock H-PSS solution was then used to adjust the pH of the capsule suspension.

Methods. *Polyelectrolyte Multilayer Formation.* Multilayer formation was accomplished by adsorption at 10^{-2} monoM bulk concentrations of PAH or PSS in 0.5 M NaCl with three repeated centrifugation cycles in water as the washing procedure. Details of the procedure are described elsewhere.[11] The particle concentration in the dispersions was kept low (0.1 w %) to avoid bridging coagulation.

Formation of Hollow Polyelectrolyte Shells. After the desired number of 13 layers were deposited, the particles were exposed to 0.1 M HCl for 5 min. During this time period the melamin resin core was dissolved and diffused out of the particle interior without disrupting the polyelectrolyte layers. Some FITC-labeled rest remained inside. Figure 2 provides a confocal micrograph showing that the label is homogeneously distributed inside the capsule walls. (The brighter fluorescence in the center is an artifact that is explained by the focusing properties of the spherical shell on the light reflected from the lower hemisphere's interface.) In other cases, the labeled melamin remained in the form of small spheres inside the larger capsule.
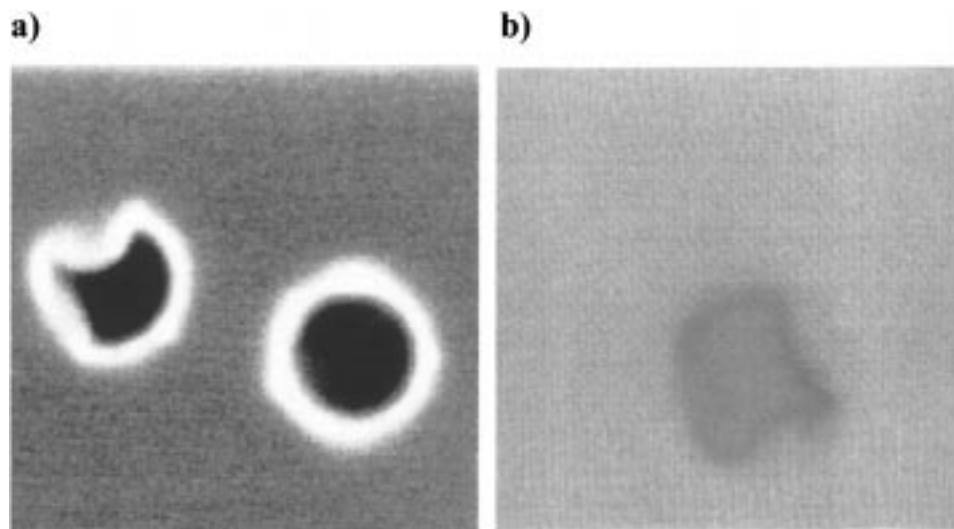
Figure 3. Confocal microscopy images of hollow polyelectrolyte capsules consisting of 13 PSS/PAH-FITC layers in the presence of PAH-FITC (a) and 6-CF (b) in the bulk solution.

Fluorescence Spectroscopy. Fluorescence spectra were recorded by means of a Fluorolog, Spex. Excitation was set to 492 nm.

Confocal Microscopy. The micrographs were obtained by means of a Leica confocal scanning system mounted to a Leica Aristoplan. A 100× oil immersion objective was used. The standard filter settings for fluorescein excitation and emission were used. Equal volumes of the capsule suspension and the labeled polyelectrolyte solution (PAH) were mixed and incubated for 30 min prior to the microscopic observation. A 17 μL aliquot of the sample was transferred onto standard microscope slides. When capsules with a negative surface charge had been examined, the microscope slides were coated with poly(ethylenimine) (PEI) by dipping them for 1 min into a 1 mg/mL PEI solution. Rinsing in water and ethanol was sufficient to remove excess PEI. This coating procedure ensured adhesion of the negative shells to the surface of the microscope slide, thus avoiding Brownian motion during the procedure of signal accumulation while scanning. Cover slips were mounted with nail lack. When the bulk solution contained 6-CF, the field of view was bleached prior to the microscopic examination by applying a scan with high laser power.

Results and Discussions

Permeability of Capsule Walls. The permeability of polyelectrolyte microcapsules for polymeric species and for 6-CF has been studied by means of confocal microscopy. A solution of FITC-PAH, MW 50 000, was mixed with shells composed of 13 PSS/FITC-PAH layers to give a final concentration of 0.5 mg/mL. Figure 3a demonstrates that the permeability of the shell walls for the high molecular weight PAH-FITC (MW 50 000) is so small that over 20 min no fluorescence was observed in the capsule interior. It is further remarkable that polymer exclusion is observed regardless of whether the capsules are deformed (left part of Figure 3a) or not. This picture is typical and was observed for the capsule population in general. In contrast, 6-CF penetrates the shell walls easily. Fluorescence from both of the exterior and the interior of the capsules (Figure 3b) is recovered within 1 min after bleaching. Due to the fast penetration it was not possible to record any kinetics of the fluorescence recovery of 6-CF given the time resolution of the scan. By means of quenching studies and Förster energy transfer experiments, it has been shown recently that polar fluorescent
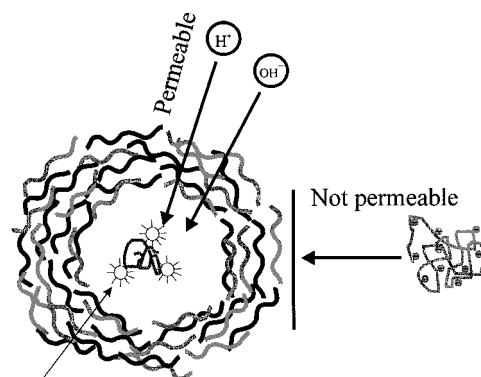
Fluorescent pH sensing Label

Figure 4. Schematic representation of the Donnan equilibrium situation developing in the presence of bulk polymeric acid not capable of penetrating the walls of the hollow polyelectrolyte capsules.

labels penetrate polyelectrolytes assembled on flat surfaces and Rhodamin B doped melamin formaldehyde particles.[12−14] In summary, it can be concluded that these multilayer polyelectrolyte capsule walls have semipermeable properties excluding higher molecular weight molecules but allowing diffusion in lower molecular weight polar species, such as 6-CF with a molecular weight of 376. Confocal microscopy further revealed that in the presence of 10 mg/mL Na-PSS of MW 70 000 the capsules were fully collapsed as a result of osmotic shrinkage. (These experiments were performed, however, with shells obtained from different templates with no melamin remaining inside.) All these observed features ensured that the capsules represent a model for the experimental observation and the theoretical consideration of the Donnan equilibrium of ionic permeating species induced by polyelectrolyte exclusion. A theoretical description of the Donnan equilibrium and the accompanying experimental investigation of this situation follows next.

Donnan Equilibrium for Hollow Polyelectrolyte Capsules: Theory. *The Model.* The model consists of a two-compartment system separated by the semipermeable polyelectrolyte shell wall, Figure 4. The capsule wall is assumed to be permeable for water, hydrogen ions, hydroxyl ions, and small salt ions. It is considered impermeable for polymeric solutes, such as the polyanions outside and melamine formaldehyde

polymers, which eventually have remained inside as a result of the capsule fabrication procedure.

The equations used for the quantitative description of the model are based on two assumptions. First, a Donnan equilibrium distribution of all permeable ion species, in particular protons and hydroxyl ions, between the two compartments is assumed. This implies that the concentration of these ions is different in both phases due to the presence of a negatively charged polymeric solute in the external solution. Second, the nonnegligible excess of electric charge in the capsule interior is considered. This excess charge is localized in the capsule interior part of the electric double layer. The last assumption differs from the conventional treatment of a Donnan equilibrium situation found in textbooks. There, quasi-electroneutrality in both phases is the starting point for the derivation of the corresponding equations, because, indeed, for macroscopic phases the deviation from electroneutrality caused by the Donnan potential difference is negligibly small. However, in the situation of a small interior volume together with low ion concentrations, deviations from electroneutrality cannot be considered small compared with the effect caused upon the pH. This becomes obvious if one considers for a moment strict observation of electroneutrality in the interior. In the absence of any other small ions except hydrogen and hydroxyl ions, this would immediately yield the trivial answer that the pH in the interior should be always equal to 7, regardless of the pH of the bulk solution. This conclusion is in striking discrepancy with the experimental results. The deviation from electroneutrality, that is the net charging of the interior phase ΔQ, can be calculated from the capacitance of the system C and the Donnan potential difference $\Delta \phi$.

$$\Delta Q = C \Delta \varphi \qquad (1)$$

The capacitance of the shell is given by its geometrical parameters such as the surface S and the ion concentrations, $c_{A,K}$, which also define the Debye length κ^{-1}

$$\kappa^{-1} = \sqrt{\frac{\epsilon \epsilon_0 R T}{F^2 \sum\limits_{A,K} (c_A + c_K)}} \qquad (2)$$

F, R, and T denote Faraday's constant, the gas constant, and absolute temperature. ϵ and ϵ_0 denote the relative and absolute dielectric constants. The summation in eq 2 is carried out over all monovalent ionic species, anionic and cationic, including hydrogen and hydroxyl ions, present in the capsule interior. The capacity for a flat plate condensor reads

$$C = \epsilon \epsilon_0 \frac{S}{\kappa^{-1}} \qquad (3)$$

In eq 3 it was assumed that, since ions penetrate the shell wall easily, the Debye length provides the effective distance between the condensor plates. This assumption holds at least for thin shell walls and capsules suspended in low background electrolyte concentrations, that is for the conditions under which the experiments have been performed. It holds if the capsule radius r is larger than the Debye length and the latter is larger than the capsule wall thickness, but it is easy to modify eq 3 if these conditions are not met. In eq 3 it was further assumed that the Debye length in the exterior phase is much smaller than in the interior solution. This assumption can be justified by the presence of the polyanions. Indeed, the polyionic nature of the

charged species implies that their energy in the electric field near the surface is much larger than kT, thus giving rise to a very small Debye length outside.

The Donnan equilibrium distribution of any monovalent cationic and anionic species including hydrogen and hydroxyl ions, K and A, respectively, is given as

$$\frac{c_{K^+}^i}{c_{K^+}^o} = \frac{c_{A^-}^o}{c_{A^-}^i} = \exp\left(-\frac{F \Delta \varphi}{R T}\right) \qquad (4)$$

where indices i and o stand for the internal and external compartment, respectively. The Donnan potential difference $\Delta \phi$ is defined as the difference between the inside and outside phases. Equation 4 can be easily extended to the case of ions with an arbitrary valency.

The excess of the electric charge in the interior is given by the difference in the concentration of all anionic and cationic species present in the internal solution. According to eq 1 it can be expressed as an electric charge accumulated in the electric double layer system, whereby the electric potential difference of this system is taken as the Donnan potential. Naturally, the ion concentrations assume a Boltzmann distribution over the electric double layer. Concentrations are therefore taken as average values in each compartment.

It follows

$$\sum\limits_{K,A} (c_{K^+}^i - c_{A^-}^i) F V = \frac{\epsilon \epsilon_0 S}{\kappa^{-1}} \frac{R T}{F} \ln \frac{c_{H^+}^o}{c_{H^+}^i} \qquad (5)$$

V is the volume of the internal solution of the hollow polyelectrolyte shell.

It is worthwhile to note that the monomeric concentration of the nonpenetrating polyelectrolyte solute in the bulk solution determines the external pH. Namely, for the infinite bulk phase, macroscopic electroneutrality has be assumed, which reads

$$\sum\limits_{K} c_{K^+}^o = \sum\limits_{A} c_{A^-}^o + Z_{P^-} c_{P^-}^o \qquad (6)$$

The summations in eq 6 are carried out over all monovalent anionic, A, and cationic species, K, including hydrogen and hydroxyl ions, respectively. Z_{P^-} is the negative charge of a monomeric unit of the polyanion present in the bulk. The assumption of an infinite external compartment corresponds to a low concentration of capsules in dispersion during experiments. Thus, the external conditions with respect to pH and salt concentration are known.

According to

$$c_{H^+} c_{OH^-} = 10^{-14} \qquad (7)$$

the external as well as internal concentration of hydroxyl ions can be substituted by the corresponding concentration of hydrogen ions. Further, taking into account eq 4, one can express the internal concentration of other ionic species by the internal concentration of hydrogen ions, i.e., inner pH. And, finally, assuming a constant surface area and a constant volume of the polymeric hollow capsules, eq 5 can be solved with regard to the pH of the capsule interior. In this way, one may calculate a dependence of the inner pH on the external pH. However, in this case one would have to assume that an osmotic pressure difference between the two compartments can be compensated by the mechanical resistance of the polyelectrolyte shell.

The further development of the theoretical description considers the case in which the encapsulated volume changes to compensate for the initially different osmolarities on both sides of the shell wall. However, the surface area of the polyelectrolyte capsules remains constant. This means that such a situation can account only for the case when the encapsulated volume is either smaller than or at least equal to the volume of a sphere with the same surface. Hence, we assume an osmotic balance between the two solutions. The corresponding relation reads

$$\sum_{K,A}(c_{K+}^{i} + c_{A-}^{i}) + \frac{n_{P}^{i}}{V} = \sum_{K,A}(c_{K+}^{o} + c_{A-}^{o}) + c_{P-}^{o}\frac{M_{P-}^{m}}{M_{P-}^{P}} \quad (8)$$

The osmotic contribution of some remaining melamin resin polymers in the interior is explicitly taken into account in terms of its molar number n_P. The osmotic contribution of the polyanion in the bulk solution is expressed by its monomeric concentration c_{P-}^{o} multiplied by the ratio of the molecular weights of a monomer and a polymer, M^M and M^P, respectively. Other terms in eq 6 describe osmotic contriburions of permeable ionic species.

After substituting internal concentrations of ionic species by external ones as well as by the internal hydrogen ion concentration, as it is introduced above, one can combine eqs 4−8 into two concomitant equations that then represent a system of two nonlinear equations for the two unknown variables, the volume V and the internal hydrogen ion concentration. This system of equations can then be solved by a numerical iteration procedure. In the next section the experimental data will be compared with the predictions of the theoretical model.

Donnan Equilibrium for Hollow Polyelectrolytes Capsules: Experimental Results. Experimental observations of the above theoretically described situation were conducted on 3.3 μm hollow polyelectrolyte capsules containing in the interior the pH-dependent fluorescent marker fluorescein bound to residual melamin formaldehyde polymers. A suspension of polyelectrolyte capsules was titrated with H-PSS of different molecular weights. The bulk pH was monitored by means of a microelectrode, while the inner pH was derived from the fluorescence intensity of fluorescein. The control experiment consisted of titrating the suspension with HCl instead of using polyanions. It was already shown above that the shell walls are readily permeable for 6-CF. Therefore it was assumed that the smaller chloride ions (and naturally the hydrogen ions) also penetrate the capsule walls. Hence, it can be concluded that the titration with HCl results in an equilibrium distribution of hydrogen ions on both sides of the capsule wall. The fluorescence was recorded in relative units with respect to the reference value of the fluorescence at a pH value of 5.5. This pH corresponds to the initial pH of the solution.

Figure 5 shows that, regardless of the molecular weight of H-PSS varying within the range 4200−70 000, the titration of the capsule suspension produced fluorescence vs bulk pH curves that were clearly different from the fluorescence curve of the control, i.e., titration with HCl. The behavior of the fluorescence when it was titrated with H-PSS is as follows: The fluorescence decreases with decreasing bulk pH, but there is always a shift of about 1.2 pH units between the control and the curves obtained by titration with the polyanions. In this case a more acid bulk pH was required to yield the same fluorescence decrease as in the case of titration with HCl. These data lead to the conclusion that the pH of the capsule interior is by approximately one pH unit more basic than the pH of the bulk.
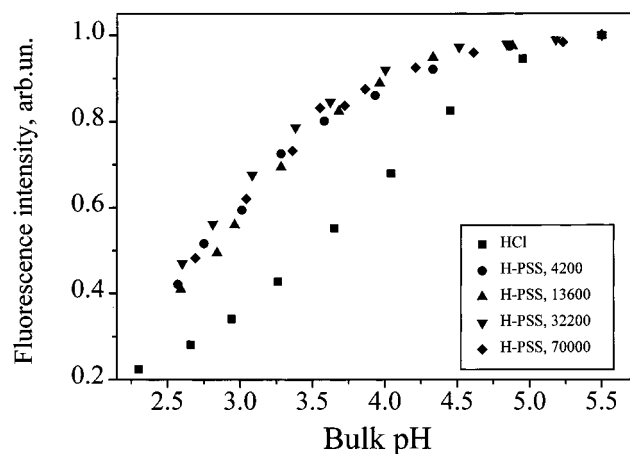

Figure 5. Fluorescence intensity of a suspension of polyelectrolyte capsules containing 6-CF as a fluorescent marker vs the bulk pH titrated by means of H-PSS and HCl. Different symbols as described in the inset refer to either various molecular weights of H-PSS or HCl, respectively.
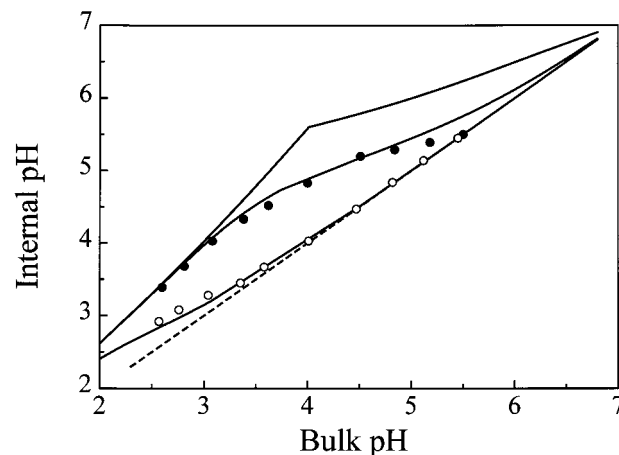

Figure 6. Comparison of the experimentally obtained inner pH with theoretical predictions as a function of bulk pH titrated with H-PSS (MW 4200) in the absence of salt (solid circles) and in the presence of 1 mM NaCl (hollow circles). The dashed line indicates the control obtained by titrating the capsule dispersion with HCl. Parameters for the theoretical curves were melamin resin concentration 10^{-4} M and capsule radius 3 μm. The background monovalent electrolyte concentration was 0 M (upper curve), 10^{-6} M (middle), and 10^{-3} M NaCl (lower curve).

This difference is attributed to the Donnan distribution of hydrogen ions between the two phases caused by the presence of impermeable polyanions in the bulk. It is further worthwhile to mention that the interior pH nevertheless decreased when the bulk pH was lowered. From the simple consideration of electroneutrality inside the capsules one would (as mentioned above) rather expect a constant pH inside. Another information is that almost no kinetics of fluorescence was recorded in the presence of polyanions when measuring the fluorescence as a function of time. This observation led to the conclusion that at least within 1 h no significant diffusion into the capsule occurred for polyanions with various molecular weights. The establishment of the proton equilibrium as judged from the fluorescence change upon H-PSS addition was so fast that it was not possible to record any fluorescence changes beyond the time of mixing.

In Figure 6 the data of Figure 5 were recalculated in terms of the inner pH vs bulk pH. The control curve for HCl is presented thus by a straight line with a slope of 1. At any pH lower than 5.5 the capsule interior was more basic than the bulk solution, which contained H-PSS. When the pH was lowered

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below 5.5, the initially small difference between external and internal pH increased, saturating at a final shift of approximately 1.2 pH units.

To study the effect of a background electrolyte on the Donnan equilibrium, 1 mM NaCl was added. It can be seen in Figure 6 that the presence of 1 mM salt inhibited the polyanion-induced pH difference between both phases down to a pH of 4. Only at still lower bulk pH was a more basic interior recorded. The maximum difference in pH was reached at the lower limit of titration, where an internal pH value of 2.9 corresponded to the bulk pH of 2.9. It is worthwhile to note that at a bulk pH value of 3 the proton concentration is just equal to the background NaCl concentration. The conclusion was that only at such low pH values was the background electrolyte concentration of 1 mM not sufficient to keep the Donnan potential negligibly small. Consequently, a pH difference reappeared.

The three solid curves in Figure 6 are theoretical curves that were obtained by assuming an inner melamin formaldehyde concentration of 0.1 mM and three different salt concentrations (0 M, 10^{-6} M, and 10^{-3} M NaCl). The two lower curves nicely fit the experimental data obtained in the absence and presence of NaCl. The theoretical curve calculated for zero salt concentration does not describe the experimental data; however, it demonstrates in an instructive manner how the osmotic shrinkage of the encapsulated volume influences the pH of the interior (see below).

The background electrolyte concentration determines the range where the inner and the bulk pH branch off. In the case under consideration the background electrolyte concentration of 10^{-6} M could correspond to trace amounts of ions. It is likely due to carbon dioxide dissolved in the samples. It is reasonable to assume that the capsules contain a rest of melamin formaldehyde as an inner impermeable polymeric species. Due to its osmotic contribution the capsules are prevented from shrinking until the osmolarities of the externally added polyion together with its counterions do not exceed that of the melamin inside.

When the capsules reduce their volume at constant surface area, the essentially constant capacity at a given Donnan potential difference $\Delta\phi$ permits inside larger concentration differences between anions and cations, respectively (see eq 5). This means in terms of pH that the internal pH can parallel the adjusted bulk pH and will not grow above a certain limit provided by the osmotic contribution of the melamin formaldehyde inside. (It was mentioned above that shrinkage of the capsules was directly observed by means of confocal microscopy when an impermeable polyion was added to the bulk solution.)

Summarizing, the behavior of the pH of the capsule interior and its volume can be described as follows. Until the excess osmolarity of the interior melamin formaldehyde is larger than the bulk osmolarity, the capsules stay expanded and an increasing pH difference with decreasing bulk pH is created upon addition of H-PSS. If, however, the H-PSS monomer concentration starts to exceed the osmolarity of the impermeable component encapsulated in the interior, shrinkage of the capsules is induced. This would lead to a reduction of the pH difference between the inside and outside. It can be concluded that there is at any given internal osmolarity an optimum bulk pH where the pH difference is largest. On one hand, it would be desirable for practical purposes to have a high concentration of an osmotically active impermeable component inside in order to produce large differences in pH. On the other hand, this would produce at low external osmolarities a large stress on the shell wall. For the capsules under study it is clear that the melamin formaldehyde concentration is sufficiently small, because the

shell suspension has undergone six washings in water. Otherwise the capsules would have already ruptured during their preparation. No evidence for that has been detected so far.[10]

The effect of 1 mM NaCl (or even higher salt concentrations) can be described as follows: It was just discussed that apart from the capacity of the shell wall the inner net charge ΔQ depends on the Donnan potential difference (see eq 1). Now, at higher background electrolyte concentrations a relatively small difference between their bulk and interior concentration is sufficient to match the conditions of eq 1. And, according to eq 4, their ratio produces thus a small Donnan potential. This leads to the breakdown of the pH difference. Only if the hydroxyl ion concentration is of the order of the background electrolyte concentration can measurable pH differences between capsule interior and bulk be created. It is also worthwhile to mention that the breakdown of the pH difference caused by the addition of salt proves the initial assumption that the capsule wall is permeable for both chloride and sodium ions.

An uncertainty that may be present in treating the system is that an effect of charges of the melamin formaldehyde remaining inside has not been explicitly taken into consideration. They may have a certain buffer capacity influencing the internal pH. Unfortunately, at present this cannot be independently assessed because the control already includes the effect of all internal melamin formaldehyde charges.

Conclusion

Hollow polyelectrolyte capsules formed by the stepwise adsorption of polyelectrolyte molecules onto colloids and by the subsequent removal of the colloidal core exclude H-PSS at least from a molecur weight of 4200 upward but are permeable for small ions. This can be employed to create differences in the pH between the interior solution and the bulk. A Donnan equilibrium situation is established upon addition of impermeable polyelectrolyte molecules to the bulk phase. The produced differences in pH depend on the capsule size. However, osmotic shrinkage of the capsules caused by the presence of the bulk polyions limits the free volume available. To compensate for this less desirable effect, one may consider encapsulating a nonionic but osmotically active impermeable species inside. Strategies are under way to achieve this particular task. The fabricated system of hollow semipermeable capsules may find interesting applications in various areas of science and technology, where a selective ion composition for controlled chemistry in spatially restricted volumes is desirable.

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