Base−Acid Equilibria in Polyelectrolyte Systems: From Weak Polyelectrolytes to Interpolyelectrolyte Complexes and Multilayered Polyelectrolyte Shells

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ABSTRACT: We have measured potentiometric titration curves of the weak polyelectrolytes, PAH[1] and PAA, interpolyelectrolyte complexes PAH−PAA, PDADMAC−PAA, and PAH−PAA, prepared by mixing of the polyelectrolyte solutions, and multilayered microcapsules made by layer-by-layer adsorption of the same pairs of oppositely charged polyelectrolytes onto $CaCO_3$ microspheres—$(PAH/PAA)_5$, $(PDADMAC/PAA)_5$, and $(PAH/PSS)_5$. The data were analyzed within the frame of an Ising model taking into account the nearest-neighbor interaction between proton binding sites. The anticooperative character of proton binding with PAH (cooperativity parameter $q = 0.13$) was shown to become a highly cooperative process in the interpolyelectrolyte complex PAH−PSS and multilayered microcapsules $(PAH/PSS)_5$, $q \approx 2-3$. The cooperativity of the process is increased also for complexes PDADMAC−PAA and PAH−PAA and for multilayered shells $(PDADMAC/PAA)_5$ and $(PAH/PAA)_5$; however, the cooperativity parameter q remains below unity for the PDADMAC−PAA system or a little higher than unity for the PAH−PAA system, indicating their much lower stability in comparison with the classical PAH−PSS system. The apparent pK values of PAH and PAA shift approximately 2−3 units to alkaline (PAH) or to the acidic (PAA) region both in multilayered microcapsules and in their stoichiometric complexes with oppositely charged polyelectrolytes. No essential difference was found between proton binding patterns of multilayered polyelectrolyte microcapsules and interpolyelectrolyte complexes.

Introduction

The interaction of oppositely charged polyelectrolytes in aqueous solutions results in the formation of so-called interpolyelectrolyte complexes (PECs) which represent an important class of macromolecular self-assembled systems very interesting from both fundamental[2] and applied[3] viewpoints. Though different interactions, such as electrostatics (predominant), hydrogen bonding, van der Waals forces, hydrophobic interactions, and others, contribute to the stability of these complexes, the driving force for the overall process is determined (in terms of thermodynamics) by a favorable entropy change due to release of low-molecular-weight counterions upon complex formation.[2a,c] The structure and properties of PECs are strongly dependent on the chemical nature of interacting polyelectrolytes, the initial ratio of their concentrations, the physicochemical properties of the solution, such as pH, ionic strength, and temperature, and the technology of their preparation. Two different types of polyelectrolyte complexes are usually obtained by appropriate choice of experimental conditions, i.e., water-soluble nonstoichiometric PECs forming stable optically transparent solutions and water-insoluble stoichiometric PECs, which either precipitate in water or exist as homogeneous turbid colloidal systems without phase separation.

The aggregates of PECs formed in water surroundings upon mixing the solutions of polycations and polyanions are amorphous in structure and usually do not reveal any order in spatial disposition of polymeric chains. A decade ago, a new type of PEC systems was developed in which a regularity of spatial arrangement of polycations and polyanions was achieved at least in one direction. An alternative layer-by-layer (LbL) technology of sequential deposition of oppositely charged polyelectrolytes onto flat macrosubstrates, developed by Decher and Hong,[4] has resulted in a burst of studies on the designing, structure, and properties of multilayered polyelectrolyte films (for a review, see ref 5) which can be considered as a special kind of PECs with ordered molecular architecture. A powerful impetus to the studies in this field was gained after extension of the LbL technology for the construction of multilayered polyelectrolyte micro- and nanocapsules by consecutive adsorption of oppositely charged polyelectrolytes onto colloid-sized organic and inorganic core particles followed by core decomposition and removal.[6] Like the flat multilayered polyelectrolyte films, these new objects are a kind of specially constructed PECs with promising potential for application in biotechnology, medicine, industry, and other fields as microcontainers, microreactors, drug delivery systems, microbatchers for controlled release of biologically active substances, and so forth.[7]

The possibility to control the physicochemical properties of capsules, first of all the permeability of their walls, is an important prerequisite for their practical usage, and it is not surprising that many studies have been devoted to characterization of the capsule permeability to the species of different molecular size (from inorganic ions to low-molecular-weight organic substances and high-molecular-weight proteins and polysaccharides) and revealing the factors governing this

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process.[7c,d] Various physicochemical factors, like ionic strength,[8a,e,9] pH,[8a,10] temperature,[11] and solvent polarity,[12] were shown to effect the permeability of the capsule walls, though the molecular mechanisms underlying the effects have been poorly understood up to now. It seems indisputable that the experimental approaches, which allow to get and to analyze the information coming from inside of the shell wall, should be used to solve the fundamental problems of capsules permeability. These can be different methods like fluorescent and spin probes, microcalorimetry, and any others sensitive to structural rearrangements of polyelectrolyte multilayers or to the changes in their dynamic characteristics.

In the present work, we address the problems of pH effect on the permeability of hollow multilayered polyelectrolyte microcapsules using a base−acid titration as the main experimental approach. Hydrogen ions are considered here not only as one of the well-known factors for effective control of the permeability of microcapsule walls[8a,10] but also as the simplest probes sensitive to the structural changes of polyelectrolyte multilayers. Indeed, it has been well demonstrated now[13] that the proton binding patterns (i.e., titration curves) for polyprotic systems even with chemically equivalent ionizable functional groups are highly dependent on the mutual arrangement of these groups due to different, depending on geometry, contribution of Coulombic interactions between binding sites to proton binding parameters and because of the binding statistics. This is the reason for essential differences found in titration behavior of linear, dendritic, comblike, and randomly branched polyelectrolytes as well as of systems with planar disposition of ionizable groups. We have studied the titration behavior of pure polyelectrolytes (PAH, PAA), polyelectrolyte complexes (PAH−PSS, PDADMAC−PAA, PAH−PAA), and corresponding multilayered polyelectrolyte microcapsules $(PAH/PSS)_5$, $(PDADMAC/PAA)_5$, and $(PAH/PAA)_5$, keeping in mind that they are the typical representatives of polyprotic systems with different spatial arrangement of ionizable groups, and the comparative study of base−acid equilibria in these systems is an important step in elucidating the molecular mechanisms of pH effect on the permeability of multilayered polyelectrolyte shells.

Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, MW∼ 70 kDa), poly(allylamine hydrochloride) (PAH, MW ∼ 70 kDa), poly(acrylic acid) (PAA, MW∼ 450 kDa), and poly(diallyldimethylammonium chloride) (PDADMAC, MW∼ 400 kDa, 20% solution in water) were purchased from Sigma-Aldrich. Sodium chloride, sodium hydroxide, and hydrochloric acid were obtained from Roth (Germany). Calcium chloride hexahydrate and ammonium bicarbonate of reagent grade quality were purchased from Reakhim (Russia). All chemicals were used without additional purification. Double quartz distilled water or the water with specific resistivity higher than 18.2 MΩ cm purified in a three-stage Milli-Q Plus 185 purification system was used in all experiments.

Preparation of $CaCO_3$ Microspheres. Morphogenesis of calcium carbonate microparticles has attracted much attention of researchers.[14] A variety of procedures for the preparation of rather uniform $CaCO_3$ microparticles (including spherical ones) were described differing in source of Ca^{2+} and CO_3^{2-} and usage of various additives to the reaction mixture, like ions of bivalent metals, proteins, synthetic polyelectrolytes, and others. They differ by methodical complexities, reproducibility, and the quality of obtained $CaCO_3$ microparticles. We have developed and used here a simple and reproducible method for preparation of spherical $CaCO_3$ microparticles with a rather narrow size distribution. It was achieved by mixing equal volumes of concentrated (0.33 M) water solutions of $CaCl_2 \cdot 6H_2O$ and Na_2CO_3 at room temperature, resulting in a rapid creation of high supersaturation relative to $CaCO_3$, i.e., $[Ca^{2+}] \cdot [CO_3^{2-}] \gg K_{sp}$, where K_{sp} is the solubility product of $CaCO_3$. The formation of $CaCO_3$ microspheres was shown to be a complicated process consisting of several consecutive stages. They include rapid formation of initial nuclei in a supersaturated solution and their growth to nanosized primary particles which aggregate further into spherical microparticles with rather complicated inner structure.[15] Aliquots (25 μL) were taken from the reaction mixture and analyzed under a light microscope. After the $CaCO_3$ microspheres reached the necessary size, the reaction was stopped by rapid filtration through a membrane filter followed by thorough washing of the precipitate with water. Microspheres of $CaCO_3$ with an average diameter 3.7 μm were used in this study.

Polyelectrolyte Complex Preparation. Complexes of (PAH−PSS), (PDADMAC−PAA), and (PAH−PAA) were prepared at 22 °C by adding solution of first polyelectrolyte under gentle stirring to the solution of the second polyelectrolyte up to the desired monomer unit molar ratio of 1:1 or 1:0.8. Both initial polyelectrolyte solutions were prepared either in water or in 0.5 M NaCl. Titration was performed after 1 day of complex incubation.

Polyelectrolyte Shell Deposition. The assembly of multilayered polyelectrolyte shells onto $CaCO_3$ microspheres was accomplished by consecutive adsorption of oppositely charged polyelectrolytes from their solutions (concentration 2 mg/mL) in 0.5 M NaCl at pH 7.0. Typically, 75 mL of polyelectrolyte solution was added to 1.5 g of dry $CaCO_3$ microparticles (the resulting particle concentration 2%, w/w), and the suspension was gently agitated on a magnetic stirrer for 15 min. Then the suspension was centrifuged at 2000 rpm for 5 min, and the precipitate was washed three times with 75 mL of 0.1 M NaCl at pH 7.0. The same procedure was repeated with polyelectrolyte of opposite charge, resulting finally in the desired number of deposited polyelectrolyte layers. Thus, the multilayered shells of PAH−PSS, PDADMAC−PAA, and PAH−PAA were deposited on $CaCO_3$ microparticles, in all cases starting with a polycation as the first layer because of the negative charge of the surface of $CaCO_3$ microparticles. The decomposition and removal of the $CaCO_3$ core resulting in hollow multilayered polyelectrolyte microcapsules were accomplished by multiple treatment of polyelectrolyte multilayer-coated $CaCO_3$ microparticles with ethylenediaminetetraacetic acid (EDTA) which forms a strong, water-soluble hexadentate Ca^{2+}−EDTA complex with stability constant about 2 orders higher than the solubility product of $CaCO_3$. The remainder of the Ca^{2+}−EDTA complex was removed from the suspension of polyelectrolyte shells by multiple washing with 0.5 M NaCl after full dissolution of $CaCO_3$. Mild conditions for core dissolution and the possibility to get pure multilayered polyelectrolyte shells free of any remains of core in the shell interior are the advantageous feature of $CaCO_3$ in comparison with MF and PS microparticles traditionally used for preparation of multilayered shells. It should be noted that multilayered polyelectrolyte shells made of different polyelectrolyte pairs reveal different reactions, depending on the ionic strength and pH of the surrounding medium. While multilayered microcapsules made of PAH−PSS are rather stable in a wide range of pHs and NaCl concentrations, microcapsules of PAH−PSS and PDADMAC−PAA are extremely sensitive to the environmental conditions and may not only aggregate but even collapse with time into disordered PEC, as it was observed for $(PDADMAC/PAA)_5$ shells. The high sensitivity of PDADMAC−PAA and PAH−PSS multilayers, deposited onto the solid flat substrates, to the ionic strength and pH of the medium has been demonstrated by Dubas and Schlenoff[16] and Shiratori and Rubner.[17] Recently, Caruso and coauthors[18] and Burke and Barrett[19] have reported on the formation of PAA/PAH multilayered shells on polystyrene and melamine formaldehyde particles[18] and colloidal silica,[19] and

the very important influence of pH and ionic strength of the medium on multilayer growth and properties has been revealed.

Potentiometric Titration. Potentiometric titration was performed on a digital, microprocessor-controlled pH-meter WTW pH 539 (Germany) using a combined glass/reference electrode, calibrated with standard buffer solutions of pH 4.0, 7.0, and 10.0. A flow of dry nitrogen was passed through the titration cell to prevent atmospheric CO_2 absorption. The titration of weak polyelectrolytes, PAH and PAA, and polyelectrolyte complexes, PAH−PSS, PDADMAC−PAA, and PAH−PAA, was performed from the alkaline region, after adjusting the pH to 11,6 with concentrated NaOH solution. 0.2 M HCl was used as the titrant, which was added with a micropipet by 20 μL portions to 15 mL of the probe with polymer concentration of 0.5 mg/mL. pH readings were always taken after establishing the equilibrium state, when the pH reached a constant value after each step of titrant addition. It was shown in separate experiments that the results are not dependent on whether titration was started from alkaline or acidic region. The starting pHs for titration of polyelectrolyte shells were chosen by taking into account their pH stability. Thus, PAH−PSS shells were titrated with 0.2 M NaOH starting from acidic region (pH 2.2) and PDADMAC−PAA shells were titrated with 0.2 M HCl starting from alkaline region (pH 11.6), while the titration of PAH−PAA shells was started from neutral region (pH 7.0) using both 0.2 M NaOH and 0.2 M HCl as titrants to cover the necessary pH range; this was done in order not to affect the possible layered organization of the multilayers. The hydrogen ion activity was corrected to the hydrogen ion concentration by using the activity coefficient determined by the Debye−Hückel approximation.[20]

Data Analysis. The titration behavior of PAH, PAA, polyelectrolyte complexes PAH−PSS, PAH−PAA, and PDADMAC−PAA as well as of multilayered shells prepared from the same polyelectrolyte pairs was analyzed using an Ising model,[21] in which the nearest-neighbor interactions between equivalent proton binding sites are considered to make the dominant contribution to the interaction energy. This model has been fruitfully used for the analysis of binding phenomena in very different systems, such as complexes of polyelectrolytes with oppositely charged surfactants,[22] helical structures formed by polynucleotides with complementary and noncomplementary monomers,[23] and many others. Two equilibrium constants, K_1 and K_2, are used in this model to describe the proton binding pattern, the first of which is the equilibrium constant for proton binding to an isolated proton-accepting site and the second one is that for proton binding to the site in close neighborhood with the already occupied one. K_2 can be expressed as product of K_1 and the so-called cooperativity parameter, q, which is a measure of the free energy of interaction between neighbor proton-accepting sites, $\Delta G = -RT \ln q$ ($q < 1$, $= 1$, and > 1 for anticooperative, noncooperative, and cooperative processes, respectively). Though rather simplified, this model, nevertheless, provides a convenient formalism for the first approximation of the proton binding process. Theoretical treatment of this model results in the following analytical expression for the titration curve of polyprotic systems:

$$\alpha = \frac{1}{2}\left\{1 - \frac{(1 - K_2[H^+])}{[(1 - K_2[H^+])^2 + 4K_1[H^+]]^{1/2}}\right\} \qquad (1)$$

where α is the degree of protonation.

Two simple equations can be obtained from the above expression:

$$K_2 = K_1 q = \frac{1}{([H^+])_{\alpha = 0.5}} \quad \text{and} \quad \left(\frac{d\alpha}{dpH}\right)_{\alpha=0.5} = -0.576\sqrt{q} \qquad (2)$$

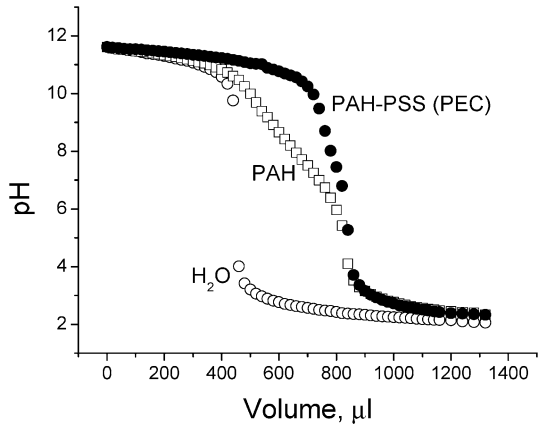

Figure 1. An example of initial curves of acid−base titration of H_2O, poly(allylamine hydrochloride), PAH, and stoichiometric complex between poly(allylamine hydrochloride) and poly(sodium 4-stirenesulfonate), PAH−PSS. Concentration of PAH is 5.35 mM in both cases (in monomer units). The titration was performed by stepwise addition of 20 μL of 0.2 M HCl starting from pH 11.6.

which were used in this work for determination of the proton binding constants K_1 and q from titration curves.

Results and Discussion

We have measured and analyzed the base−acid titration curves for the systems with chemically identical ionizable functional groups, but differing in their spatial organization (i.e., free polyelectrolytes in solution, interpolyelectrolyte complexes, and multilayered polyelectrolyte microcapsules). An example of the typical experimental titration curves is presented in Figure 1. Each experiment included the so-called blank titration of the solvent (salt-free H_2O or 0.5 M NaCl solution) and the titration of polyelectrolyte, interpolyelectrolyte complex, and multilayered polyelectrolyte shells. It is important that all conditions were kept strictly the same in each series of experiments—the same solvent, the same initial volume of titratable mixture, the same starting pH thoroughly adjusted at the beginning of the titration experiments, the titrant of the same concentration added at exactly the same portions to the titratable mixture. Under these conditions, the shift of the titration curves of PAH and interpolyelectrolyte complex PAH−PSS (Figure 1) relative to the blank titration (H_2O in Figure 1) is completely determined by proton uptake by PAH and PAH−PSS. All experimental data were then transferred into and processed in an Origin graphic program and finally transformed to the classical form of titration curves, i.e., the degree of protonation, α, vs pH (α is determined as the ratio of concentration of protonated functional groups to their total concentration). Base−acid titration of three polyelectrolyte systems was performed, and the results are discussed below.

Base−Acid Titration of PAH−PSS Systems. The results of potentiometric titration of free PAH, stoichiometric interpolyelectrolyte complex PAH−PSS, and multilayered polyelectrolyte shells $(PAH/PSS)_5$ in water and in 0.5 M NaCl are presented in Figure 2a,b. For comparison, the titration curve of the interpolyelectrolyte complex with a nonstoichiometric ratio of components, PAH−PSS (1:0.8, molar ratio of monomer units), is also plotted in Figure 2a. The only types of titratable groups in these systems are the primary amino groups of PAH, since PSS is a strong polyelectrolyte and its

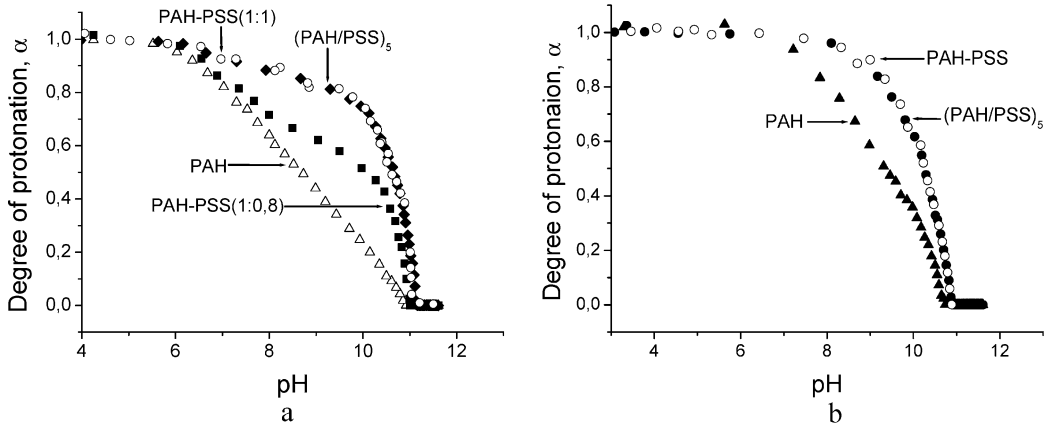

Figure 2. Curves of potentiometric titration of PAH, stoichiometric interpolyelectrolyte complex PAH−PSS (1:1), nonstoichiometric complex PAH−PSS (1:0.8), and multilayered polyelectrolyte capsules $(PAH/PSS)_5$ in (a) Milli-Q water and (b) 0.5 M NaCl. PAH concentration 5.35 mM. The titration was started from acidic region because of full dissolution of microcapsules at pH above 11.4. 0.2 M NaOH was used as a titrant.

Table 1. Proton Binding Parameters for Different Polyelectrolyte Systems Found from Appropriate Titration Curves in Accordance with One-Dimensional Ising Model Described in the Experimental Section

	solvent	q^a	$pK_{app}{}^b$
PAH	H_2O	0.13	8.7
	0.5 M NaCl	0.17	9.3
PAA	H_2O	0.13	6.45
	0.5 M NaCl	0.16	5.4
PAH− PSS[c]	H_2O	3.06	∼10.7[d]
	0.5 M NaCl	2.04	∼10.3[d]
PDADMAC−PAA[c]	H_2O	0.65	3,6
	0.5 M NaCl	0.56	4,0
PAH−PAA[c]	H_2O	1.21,[e] 1.11[f]	∼1.9,[e] ∼10.7[f]
	0.5 M NaCl	0.97[f]	∼4.3,[e] ∼10[f]

[a] Determined from the slope of titration curves. [b] $pK_{app} = -\log K_1$. [c] Both polyelectrolyte complexes and multilayered polyelectrolyte shells are assumed by this notation. [d] These values are rough estimation of pK_{app} as pH at the point of the maximal slope of titration curves. [e,f] PAA and PAH both in polyelectrolyte complex and in multilayered microcapsules PAH−PAA, respectively.

sulfonic groups are fully ionized in the pH range used in this study. The apparent pK of PAH in salt-free conditions (Figure 2a) equals 8.7, which is in good agreement with the data of Fang et al.[24] PAH behaves as apparent monobasic acid relative to proton binding, with one inflection point practically coinciding with $pK_{1/2}$ (equal to pH at which $\alpha = {}^1/_2$). However, the shape of the titration curve of PAH does not fit the classical Henderson−Hasselbach equation (eq 3, where $n = 1$)

$$\mathrm{pH} = pK_a + n \log[\alpha/(1 - \alpha)] \qquad (3)$$

describing standard sigmoidal titration curves for proton binding equilibria in single-protic systems, for all of which the same slope of titration curves at the middle point is characteristic, $(d\alpha/dpH)_{\alpha=1/2} \approx 0.576$. The slope for the titration curve of PAH is much lower and equal to 0.21, evidencing the anticooperative character of proton binding. The titration curves of polyelectrolytes, polyelectrolyte complexes, and multilayered polyelectrolyte microcapsules were analyzed within the frame of an Ising model taking into account a nearest-neighbor interaction between binding sites (see Experimental Section). Two equilibrium constants, K_{app} and q, characterizing the proton binding equilibrium for all systems studied in this work are summarized in Table 1. It can be easily shown that there is a direct interconnection between the cooperativity parameter q in eq 1 derived from the Ising model and an empirical parameter n in an extended Henderson−Hasselbach equation (3), introduced by Katchalsky and Sputnik[25] and Leyte and Mandel[26] for a description of the titration behavior of polyelectrolytes**,** i.e., $q = n^{-2}$ and $pK_1 = pK_a = pK_{app}$, which allows the direct comparison of titration parameters obtained from these two different approaches for quantitative treatment of titration curves. The value of q for PAH equals 0.13 in water (Table 1), which is in good accordance with the titration data of Kobayashi et al.[27] In 0.5 M NaCl q increases; however, it is much lower than one, evidencing that proton binding to PAH remains highly anticooperative independent of the ionic strength of the solution. The anticooperativity of proton binding to PAH is the result of the electrostatic repulsion between the newly attaching proton and the positively charged PAH, which increases with the increase of protonation degree of PAH, α. Though ionic strength exerts a rather small effect on the cooperativity of the process (q increases from 0.13 to 0.17 going from water to 0.5 M NaCl solution), it noticeably shifts the apparent pK_{app} value into the alkaline region, from 8.7 in H_2O to 9.33 in 0.5 M NaCl (Figure 2), thus facilitating the binding of protons with PAH, probably due to the partial neutralization of the electrostatic repulsion between proton-binding sites.

Drastic changes in titration behavior of PAH are observed when an equimolar concentration of PSS (in monomer units) is presented in the titratable solution. The formation of a stoichiometric polyelectrolyte complex PAH/PSS (1:1) results not only in a large shift of the apparent dissociation constant, pK_{app}, into the alkaline region but also in a high increase of the q value. It is true for the titration both in H_2O (Figure 2a) and in 0.5 M NaCl (Figure 2b). pK_{app} increases from 8.7 for pure PAH to 10.7 for the stoichiometric PAH/PSS complex in H_2O and from 9.3 to 10.3 in 0.5 M NaCl. Such shifts in pK_{app} were demonstrated both for polybases (shift to alkaline region) and for polyacids (shift to acidic region) upon formation of unordered PECs in solutions[2b,i] or highly ordered polyelectrolyte multilayers (a kind of PECs) on solid substrates.[17,28] In contrast to the anticooperative character of pure PAH titration, the titration of the PAH/PSS polyelectrolyte complex is highly cooperative, and the cooperativity parameter, q, exceeds 1 and equals 3.06 for PAH/PSS titration in H_2O and 2.04 in 0.5 M NaCl. This means that, in contrast to titration of free PAH, the proton binding in the PAH/

PSS complex is facilitated with increasing the protonation degree, α. The titration curve of the stoichiometric PAH/PSS complex is strongly asymmetric with rather protracted tails at protonation degree >0.7. The comparison of titration behavior of stoichiometric (1:1) and nonstoichiometric (1:0.8) complex PAH/PSS (Figure 2a) shows that this part of the titration curve can be attributed to the proton binding with amino groups of PAH which do not form salt linkages and remain free even in the stoichiometric PAH/PSS complex, the number of which increased in a nonstoichiometric one.

The more surprising result of this study is the finding that the proton binding patterns of multilayered $(PAH/PSS)_5$ microcapsules and stoichiometric polyelectrolyte complex PAH−PSS are practically the same and independent of ionic strength of the medium (Figure 2a,b). Taking into account a certain ordering of polyelectrolyte layers[5b] in multilayered $(PAH/PSS)_5$ microcapsules and the stochastically formed unordered structure of the stoichiometric polyelectrolyte complex PAH−PSS, one would expect some differences in titration behavior of these systems due to different contribution of Coulombic interaction between binding sites to proton binding parameters. The coincidence of the titration curves seems to evidence the absence of strong regularity in spatial disposition of titratable groups in multilayered polyelectrolyte microcapsules $(PAH/PSS)_5$ in comparison with the polyelectrolyte complex PAH−PSS. In other words, one can state that the regular alternative arrangement of polyelectrolyte layers in LbL-assembled microcapsules does not necessarily mean a regular spatial disposition of proton binding centers; rather, they are arranged irregularly and behave relative to base−acid titration much similar to stochastically disposed titratable groups in the polyelectrolyte complex PAH−PSS. Thus, it can be concluded that proton uptake and release results in similar structural rearrangements in the $(PAH/PSS)_5$ microcapsules and polyelectrolyte complex PAH−PSS, and like for disordered polyelectrolyte complex, pH changes result in swelling and shrinking of the polyelectrolyte network due to charge−charge interactions. This seems to determine the well-documented effect of pH[8a,10] on permeability of multilayered polyelectrolyte microcapsules rather than the formation of pores, like those observed by Rubner et al.[29] at special treatment (wetting and drying) of multilayered polyelectrolyte films.

Figure 3 shows the titration curves of PAH with PSS solution. The concentration of PSS was an order higher than that of PAH to minimize the effect of dilution on pH changes during titration. Despite the equality of initial pH values of PAH and PSS solutions, a consecutive increase in pH is observed with incremental addition of PSS to PAH, evidencing the proton uptake from the medium accompanying the polyelectrolyte complex formation. The ratio of concentrations of PSS/PAH at which the inflection point is observed is highly dependent on the initial pH values of polyelectrolyte solutions (Figure 3) and in general does not relate directly to the stoichiometry of the formed polyelectrolyte complex.[30] Indeed, we have demonstrated that no pH change, and, accordingly, no inflection point, is observed at incremental addition of PSS to PAH when the initial pH of both solutions equals 4. The complex formation does in this case not accompany proton uptake from the solution because PAH is already fully protonated at this pH (Figure 2a). It can be easily shown that the pH changes

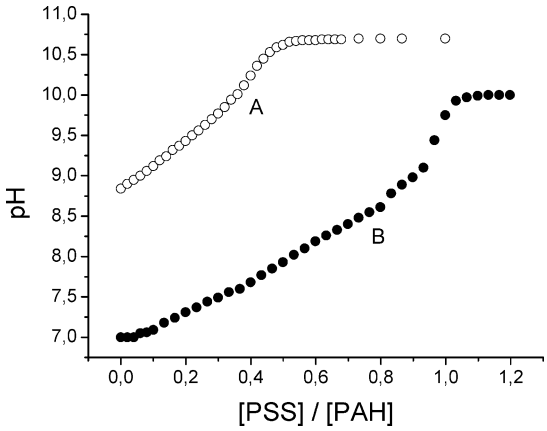

Figure 3. Potentiometric curves for the incremental addition of PSS to PAH at different initial pH of polyelectrolyte solutions, A, pH 8.8; B, pH 7.0, in water. Initial concentrations of PAH is 5.35 mM and of PSS is 53.5 mM.

found at incremental addition of PSS to PAH at different initial pH values of polyelectrolyte solutions are in quantitative agreement with base−acid titration data shown in Figure 2a. Thus, one can conclude that the formation of polyelectrolyte complex (PEC) in solution, as well as the assembling of multilayered polyelectrolyte films on solid substrates or microcapsules on colloid-sized particles (as special kind of PECs), is accompanied by proton uptake (or by proton release, as it will be shown in the next section) from the solution.

Base−Acid Titration of PDADMAC−PAA Systems. PDADMAC−PAA is a system with carboxylic groups of poly(acrylic acid) as only type of titratable groups. The curves of potentiometric titration of free PAA, of stoichiometric polyelectrolyte complex PDADMAC−PAA, and of multilayered polyelectrolyte microcapsules $(PDADMAC/PAA)_5$ in water and in 0.5 M NaCl are presented in Figure 4. Like PAH, PAA behaves as apparent monobasic acid at base−acid titration, revealing one inflection point on the titration curve practically coinciding with $pK_{1/2}$. The apparent p*K* values for PAA are 6.45 and 5.4 respectively in water and in 0.5 M NaCl and are in good agreement with the data of other authors.[27,31] In contrast to PAH, the pK_{app} of PAA decreases with rise of NaCl content in solution, which means that the formation of the ionic atmosphere around carboxylic groups of PAA makes the proton binding more difficult. The slope of titration curves at the midpoint, $(d\alpha/dpH)_{\alpha=1/2}$, is much lower of the value 0.576 predicted from classical Henderson−Hasselbach equation (3), evidencing the anticooperative character of proton binding to PAA. The cooperativity parameter, *q*, derived from the titration curves equals to 0.13 and 0.16 for titration in H_2O and in 0.5 M NaCl, respectively (Table 1). These values are very close to those for PAH and are characteristic of highly anticooperative processes.

The shift of titration curves into acidic region is observed upon complex formation of PAA with PDADMAC (Figure 4a,b). It is more pronounced in salt-free solution, where the more stable polyelectrolyte complex PDADMAC−PAA is formed due to the absence of a screening effect of ionic atmosphere. Though the proton binding to the PDADMAC−PAA complex is a more cooperative process ($q = 0.65$) in comparison with proton binding to PAA ($q = 0.13$), both processes are anticooperative ($q < 1$). Similarly to the PAH−PSS system, there is no detectable difference in titration behavior

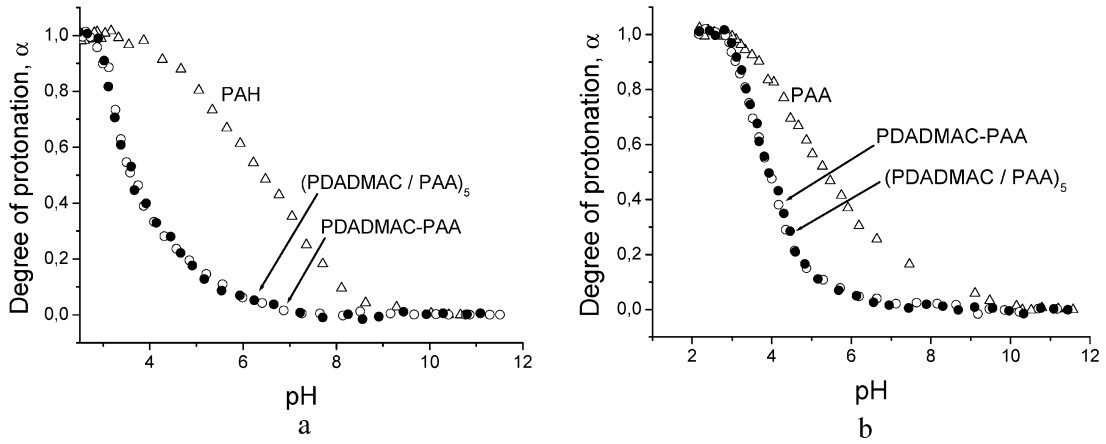

Figure 4. Curves of potentiometric titration of poly(acrylic acid), PAA, stoichiometric polyelectrolyte complex between poly(diallyldimethylammonium chloride), and poly(acrylic acid), PDADMAC−PAA, and multilayered microcapsules $(PDADMAC/PAA)_5$ in (a) Milli-Q water and (b) 0.5 M NaCl. PAA concentration is 6.94 mM (in monomer units) for all systems. The titration from alkaline region with 0.2 M HCl.

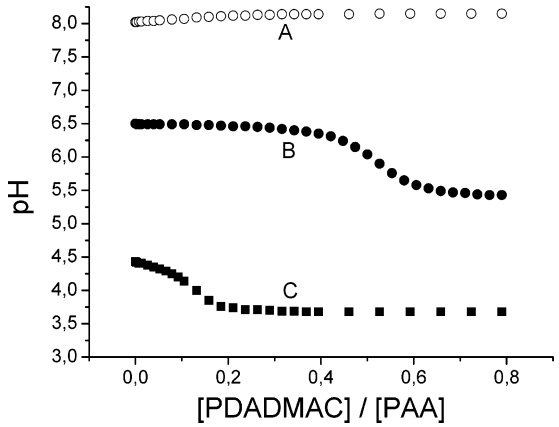

Figure 5. Potentiometric curves for the incremental addition of PDADMAC to PAA at different initial pH of polyelectrolyte solutions, A, pH 8.1; B, pH 6.5; C, pH 4.4, in water. Initial concentration of PAA is 6.94 mM, and concentration of PDADMAC is 69.4 mM.

of polyelectrolyte complex PDADMAC−PAA and multilayered microcapsules (Figure 4a,b), evidencing the absence of high order in spatial arrangement of titratable carboxylic groups in the stochastically formed polyelectrolyte complex PDADMAC−PAA and in multilayered microcapsules $(PDADMAC/PAA)_5$ with alternating packing of polyelectrolyte layers.

Figure 5 shows the titration curves of PAA with PDADMAC solution. The initial pH values of both solutions were the same. The concentration of the titrant (PDADMAC) was an order of magnitude higher of PAA concentration to exclude noticeable pH changes due to dilution. The complex formation in the PDADMAC−PAA system is accompanied, in contrast to PAH−PSS, by proton release into the surroundings, which results in acidification of the medium. The proton exclusion from the formed complex takes place at pH values where the protonation degree of PAA is rather high (for example, at pH 4.5 and 6.5, Figure 5). However, nearly no pH change is observed at incremental addition PDADMAC to PAA solution at pH 8, where PAA is practically in fully ionized form. The position of the inflection points on the titration curves is dependent on the initial pH values and is not connected directly with the stoichiometry of the complex.

Base−Acid Titration of PAH−PAA Systems. In contrast to the above two polyelectrolyte systems, which can be considered as systems with one type of proton-donor or proton-acceptor titratable groups, PAH−PAA is a more complicated system consisting of two weak polyelectrolytes where both types of titratable groups are presented. Its titration behavior is also essentially more complicated in comparison with PAH−PSS and PDADMAC−PAA systems. The potentiometric titration curves of polyelectrolyte complex and multilayered polyelectrolyte shells $(PAH/PAA)_5$ in H_2O and in 0.5 M NaCl are shown in Figure 6. For comparison, the titration curves of PAH and PAA are also reproduced at these figures. One can see two clear-cut branches of proton binding by the PAH−PAA system in alkaline and acidic regions. These branches correspond to proton binding with amino groups of PAH (alkaline region) and with carboxylic groups of PAA (acidic region). The estimated values of pK_{app} for alkaline and acidic branches of the total titration curve equal respectively to ∼10.7 and 1.9 (Table 1). The shift of about 2 pH units into the alkaline region is found for the PAH branch of the PAH−PAA complex in salt-free solution in comparison with the titration curve of pure PAH, as well as the shift of about 3 pH units into the acidic region for the PAA branch relative to the titration curve of pure PAA. An analogous shift is characteristic of the PAH−PAA system in 0.5 M NaCl. It is interesting that the cooperativity parameter, q, equals 1.11−1.21 for the titration in the salt-free medium and decreases up to 0.97 for the titration in 0.5 M NaCl. These values are close to unity, indicating nearly noncooperativity of the process. It looks like the proton binding in the PAH−PAA system is a noncooperative process with nearly full absence (or some compensation) of Coulomb interactions between nearest-neighbor proton binding sites. This noncooperativity may shed light on the numerous evidences of the high instability of the PAH−PAA multilayers, which was shown by several research groups.[29,32] As in the case of the PAH−PSS and PDADMAC−PAA systems, no differences were revealed between the titration curves of the polyelectrolyte complex PAH−PAA and multilayered polyelectrolyte shells of the same polyelectrolytes.

Figure 7 shows the titration curves of PAA with concentrated PAH at equal initial pH values of both polyelectrolyte solutions. One can see that both proton uptake and release can be observed at complex formation in the PAH−PAA system, which is determined by

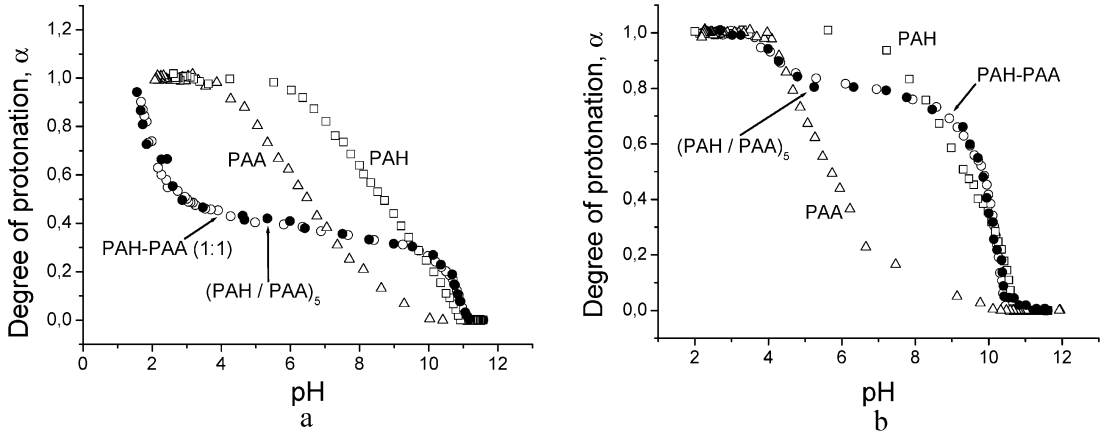

Figure 6. Curves of potentiometric titration of PAA, PAH, stoichiometric polyelectrolyte complex PAH−PAA, and multilayered microcapsules $(PAH/PAA)_5$ in (a) Milli-Q water and (b) 0.5 M NaCl. Concentration of both PAH and PAA is 5.35 mM (in monomer units). Starting pH for titration of PAH−PAA complex and $(PAH/PAA)_5$ microcapsules was 7.0. Titration was performed with 0.2 M NaOH and 0.2 M HCl from neutral to alkaline and acidic regions, respectively.

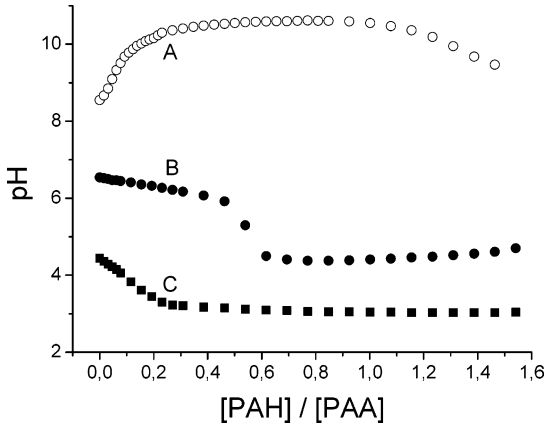

Figure 7. Potentiometric curves for incremental addition of PAH to PAA at different initial pH of polyelectrolyte solutions, A, 8.6; B, 6.6; C, 4.4, in water. Initial concentrations of PAA is 6.94 mM and of PAH is 69.4 mM.

the initial pH values of polyelectrolyte solutions. For example, if the initial pH of polyelectrolyte solutions is lower than 7, the release of protons takes place upon complex formation, while the proton uptake by the complex is observed at initial pH of solutions higher.

Conclusions

We have performed direct potentiometric measurements of base−acid equilibria in three polyelectrolyte systems: (i) PAH → PAH−PSS → $(PAH/PSS)_5$, (ii) PAA → PDADMAC−PAA → $(PDADMAC/PAA)_5$, and (iii) PAH, PAA → PAH−PAA → $(PAH/PAA)_5$ to compare the titration behavior of weak polyelectrolytes in free state, interpolyelectrolyte complexes, and multilayered polyelectrolyte shells. The multilayered polyelectrolyte shells, free of contaminations with core remains, were obtained by LbL deposition of the polyelectrolytes onto $CaCO_3$ microspheres, the advantage of which in comparison with traditionally used MF and PS particles is full dissolution in mild conditions leaving no core fragments in microcapsules. The main results of the study can be summarized as follows:

1. Anticooperative character of proton binding at base−acid titration of free PAH (the cooperativity parameter $q \approx 0.13$) changes to a highly cooperative process in the interpolyelectrolyte complex with PSS and the multilayered microcapsules ($q \approx 2-3$). The cooperativity of proton binding increases also in the complexes PDADMAC−PAA and PAH−PAA and in the multilayered shells $(PDADMAC/PAA)_5$ and $(PAH/PAA)_5$. In comparison with proton binding by PAH and PAA, however, the process as a whole remains either noncooperative or slightly cooperative respectively for PDADMAC−PAA and PAH−PAA systems. There exists a correlation between the cooperativity of proton binding and the stability of polyelectrolyte shells: the higher the cooperativity of the titration process, the more stable are appropriate multilayered shells.

2. The apparent p*K* values of PAH and PAA shift approximately 2−3 units to the alkaline (PAH) or acidic (PAA) region both in their stoichiometric complexes with oppositely charged polyelectrolytes and in multilayered microcapsules. It means that there is great analogy between the titration behavior of spatially closed micro-multilayers (multilayered polyelectrolyte microcapsules) observed in this work and base−acid equilibria in flat macro-multilayers, described in a number of recent publications.

3. No essential differences are observed between proton binding patterns of polyelectrolyte complexes and multilayered polyelectrolyte microcapsules. This is an indication of the absence, like in stochastically formed interpolyelectrolyte complex in solution, of high order in disposition of charges in multilayered microcapsules, though the alternating LbL deposition technique itself assumes some ordering in the system. Rather strong interpenetration of polyelectrolyte layers seems to be characteristic of multilayered polyelectrolyte shells, at least of those templated on $CaCO_3$ microparticles.

The results of titration studies made in this work cannot, unfortunately, elucidate the molecular mechanisms of the pH effect on the permeability of polyelectrolyte shells relative to different substances. Nevertheless, some pertinent conclusions can be drawn. The coincidence of titration curves for polyelectrolyte complexes and multilayered shells seems to exclude pH-induced formation of large discrete pores (or holes) in multilayered shells, like those observed earlier by Rubner et al.[29] at special treatment of flat PAH−PAA multilayered films. Rather, a continuous and uniform shrinking and swelling of the polyelectrolyte shells, resembling the shrinking and swelling processes in pH-sensitive hydrogels, lies in the basis of the pH effect on shell permeability.

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References and Notes

(1) Abbreviations used: polyelectrolytes, PSS = poly(sodium 4-styrenesulfonate); PAH = poly(allylamine hydrochloride); PAA = poly(acrylic acid); PDADMAC = poly(diallyldimethylammonium chloride): stoichiometric interpolyelectrolyte complexes in solution, PAH−PSS, PDADMAC−PAA, PAH−PAA; and multilayered polyelectrolyte microcapsules made of 10 consecutive layers of oppositely charged polyelectrolytes, $(PAH/PSS)_5$, $(PDADMAC/PAA)_5$, $(PAH/PAA)_5$; PEC = interpolyelectrolyte complex; LbL = layer by layer.

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