Complexes of polyelectrolytes and oppositely charged ionic surfactants

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Complex formation between a single polyelectrolyte chain and ionic surfactant molecules is studied by computer simulation of a "primitive" electrolyte model with explicit charges. The surfactant head carries a charge opposite to that of the polyelectrolyte. The neutral flexible tail is modeled by tethered hard spheres. A molecular bottle-brush architecture of the resulting polyelectrolyte-surfactant-complex is observed. The end-to-end distance of the polyelectrolyte is found to behave in a nonmonotonic fashion for increasing Coulomb coupling: it first gets stretched and then the stretching is reduced by self-assembling of surfactant molecules along the polyelectrolyte. The end-to-end distance of the polyelectrolyte in the complex is more pronounced for long surfactant tails. Upon addition of salt to the complex, ionic surfactant molecules condensed onto the polyelectrolyte are replaced by salt microions which leads to a weakening of the complex and to reduced end-to-end distance. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Solutions of polyelectrolyte chains and oppositely charged ionic surfactant molecules aggregate toward complexes due to their mutual Coulomb attraction. The resulting complexes exhibit conformational, structural, and dynamical features which are much different from that of pure polyelectrolyte and pure surfactant solutions (for reviews see Refs. 1 and 2). Therefore polyelectrolyte-surfactant mixtures have proven to provide the basis for new materials with extraordinary properties that make them interesting for a wide range of applications.[2,3] While there is an increasing number of experimental studies revealing a rich variety of different complex structures as a function of chemical nature of the polyelectrolyte, surfactant and solvent molecules,[4–15] a systematic microscopic theoretical understanding to characterize and predict different complexes is still missing.

Even the self-assembly of a *single* polyelectrolyte chain with ionic surfactants at low concentration with a full treatment of the long-ranged Coulomb interaction is far from being completely understood theoretically. Here one expects complexes exhibiting a bottle-brush structure due to strong surfactant adsorption.[3] Some previous theoretical approaches assume already from the very beginning a complete adsorption of surfactant onto the polyelectrolytes for rigid[16,17] and flexible chains, see, e.g., Ref. 18, but within all these approaches the complex structure is an input, not an output. Complex formation via a thermodynamic counterion condensation theory was recently put forward by Kuhn, Levin, and co-workers including the effect of added surfactant.[19–21] This promising theory was applied to rigid polyelectrolytes only. For semiflexible and flexible polymers, Diamant and Andelman have developed a phenomenological association theory.[22,23] Their approach, however, does not include the long range of the Coulomb interactions explicitly.

Much more work has been done in two special cases: First, if the ionic surfactant is replaced by a spherical counterion (i.e., if the surfactant tail is completely absent), computer simulation studies[24–26] and theories[27,28] have shown a polyelectrolyte swelling and a subsequent polyelectrolyte collapse for increasing Coulomb coupling. This manifests itself in a nonmonotonic behavior of the polymer end-to-end distance R as a function of the Coulomb interaction strength. Second, if for complete association of ionic surfactant polarization effects are neglected (i.e., if the dipole and any higher multipole moments of the two associated charges is neglected), another complementary special case is a neutral molecular bottle brush (or a "comb polymer"). The attachment between the side chains and the backbone can be provided by an end-functionalization of the side chains or by strong hydrogen bonds.[29,30] In this case, the polyelectrolyte configuration is getting more stretched with increasing density of the side chains. A quantitative description, however, is still under debate since different simple scaling arguments[31–33] appear to predict different quantitative behavior for the sizes of the main and side chains depending on the model used and the limit that is considered.[34]

In the present paper we perform a computer simulation study of complex formation between a single polyelectrolyte and oppositely charged ionic surfactants. While there are simulations on polymer–surfactant complexation which neglect the long-range nature of the Coulomb interactions,[35] our simulation is based on the "primitive" approach of electrolytes[36] with explicit microscopic charges on the polyelectrolyte and the surfactant heads. This traditional polyelectrolyte simulation model with explicit charges has been

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proven to be very useful in different contexts of polyelectrolyte conformations.[24–26,37–41] We supplemented this model by a tethered hard sphere description for the surfactant tail. A similar counterion model was used by Rescic and Linse[42] in the context of spherical micelle complexation. As a result, complex formation toward a molecular bottle-brush architecture is observed due to the condensation of ionic surfactant on the polyelectrolyte backbone. The complex size, as characterized by the end-to-end distance R of the polyelectrolyte backbone, is calculated as a function of the relative Coulomb coupling, the tail length, and the concentration of added salt. R turns out to be nonmonotonic as a function of the Coulomb coupling, but the Coulomb collapse with pure counterions[24–26] is significantly blocked by the excluded volume of the surfactant tails which leads to a more elongated configuration. The efficiency of blocking the collapse is augmented by increasing the surfactant tail length. Furthermore, addition of salt weakens the complex stretching, since condensed ionic surfactant molecules along the polyelectrolyte are replaced by salt counterions.

The paper is organized as follows: in Sec. II, we describe our model in detail and we present details of the simulation procedure in Sec. III. Results are given in Sec. IV and we conclude in Sec. V.

II. THE MODEL

In our "primitive" model the monomers of the polyelectrolyte, the molecules of the surfactant head and tails and the microions from the added salt are treated explicitly and constitute all particles simulated while the discrete nature of the solvent is neglected. The latter only enters in the description via its dielectric constant ϵ. The microscopic interactions between the particles are a combination of excluded volume and long-ranged Coulomb forces. In order to reduce the model parameter space, we model the excluded volume of any particles to be a hard sphere of the same diameter σ which we choose to be our basic length scale. All constituents are thus charged hard spheres. In the studies of this paper we only considered the case where all microscopic ions have the same charge $\pm qe$ with e denoting the elementary charge. This is the "minimal" model that explicitly handles the counterions and may be used to describe strongly charged, flexible polyelectrolytes.[37] It goes beyond the analytical calculations that usually neglect the individual character of the counterions.[43–46]

Connectivity within the polyelectrolyte chain and the surfactant molecules is modeled by freely jointed, tethered hard sphere beads. Subsequent beads in the same chain are tethered. The maximal bond extension is b. Hence the model would be purely entropic (i.e., temperature-independent) if all charges would be zero. In detail, the polyelectrolyte has N charged monomers which are connected. Each surfactant molecule, on the other hand, consists of n particles, namely an oppositely charged head and $n-1$ neutral tail molecules all of which are linearly jointed together. The model of polyelectrolytes and surfactant molecules is schematically shown in Fig. 1.

We use an adjacency matrix T_{ij} to denote chain connectivity. For beads i,j that are tethered $T_{ij}=1$ otherwise T_{ij}
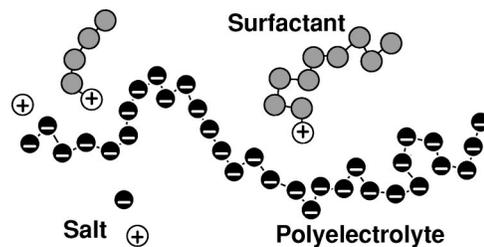
FIG. 1. Model of the polyelectrolyte–surfactant system with salt ions. Charges are indicated by "+" and "-" signs.

$=0$. With $q_i \in \{\pm 1,0\}$ denoting the charge numbers of bead i, the reduced pair interaction between any two different beads i,j at central distance r is given by

$$\frac{1}{k_B T} V_{ij}(r) = q_i q_j \frac{\lambda_B}{r} + V_H(\sigma - r) + T_{ij} V_H(r - b). \quad (1)$$

Here, the Bjerrum length $\lambda_B = q^2 e^2 / \epsilon k_B T$ sets the length scale where the Coulomb pair interaction is comparable to the thermal energy $k_B T$. Furthermore, the hard core and tether interactions are represented by the one dimensional hard wall potential

$$V_H(x) = \begin{cases} 0 & \text{if } x < 0 \\ \infty & \text{else} \end{cases}. \quad (2)$$

We note that in our notation the product $T_{ij} V_H(r-b)$ is defined to be zero if T_{ij} is zero.

To summarize, our model has the following key parameters: the number N of charged monomers of the polyelectrolyte chain, the number $n-1$ of neutral beads of the surfactant tails, the ratio λ_B/σ which measures the relative strength of the Coulomb interaction and the salt concentration c_s. In the following we shall explore the parameter space by changing n, λ_B/σ, and c_s while keeping fixed the particle hard-core diameters, the microion charges q_i, the monomer number $N = 32$, and the maximal tether length $b = 1.5\sigma$.

III. SIMULATION TECHNIQUE

We simulate the single polyelectrolyte chain of N charged beads in a finite cubic box of length L with periodic boundary conditions and periodically replicated images of the charges. This produces a (small) polyelectrolyte charge density $\rho = N/L^3 = 0.001\sigma^{-3}$ which is kept fixed throughout all simulations. The periodic images are taken into account by the Lekner sum method.[47] We performed standard Monte Carlo (MC) simulations with Metropolis rates determined by the interactions given by Eq. (1).

The relaxation of the system, especially in the fully assembled bottle brush configurations is very slow. This is also known from simulations of conventional bottle brush molecules.[34] To ensure sufficient relaxation we performed $\sim 6.5 \times 10^6$ attempted MC moves per particle at each state point for $n = 5,10$, and $\sim 2.5 \cdot 10^6$ attempted MC moves per particle for $n = 1$. The acceptance ratio is roughly 0.8.

To ensure global charge neutrality, we performed simulations for a system of a single polyelectrolyte chain together
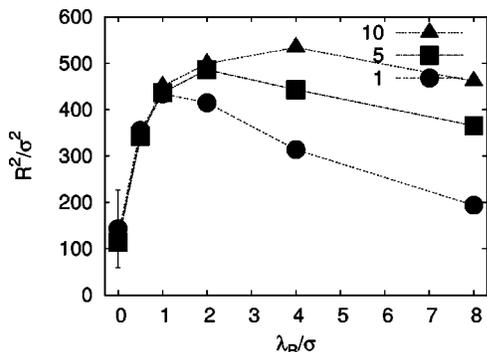
FIG. 2. The mean squared end-to-end distance R^2 as a function of the Bjerrum length λ_B for $n = 1$, 5, and 10 monomer surfactants. The statistical uncertainty is indicated by an error bar.

with $N = 32$ oppositely charged surfactant molecules. The case $n = 1$ of no tail beads at all serves as a natural reference for pure counterions. Such a situation was already studied in Ref. 37 for different Bjerrum lengths. Please note, however, that chain connectivity was modeled differently in Ref. 37 via a finite extension potential. In order to see the influence of the surfactant tail, we have further studied the cases $n = 5, 10$. In the case of added salt, we put N_s additional 1:1 salt pairs into the simulation box. Thereby a relative salt concentration of $c_s = N_s / N$ can be defined. Finally, the target quantity of our study is the end-to-end-distance R which is defined via

$$R^2 = \langle (\mathbf{R}_1 - \mathbf{R}_N)^2 \rangle, \tag{3}$$

where $\langle \cdots \rangle$ denotes a statistical average and $\mathbf{R}_1$ and $\mathbf{R}_N$ are the actual positions of the two end-monomers of the polyelectrolyte.

IV. RESULTS

A. Salt-free case

Let us first discuss the case of no added salt. As a reference situation, we have first considered the absence of any surfactant tail, i.e., $n = 1$. The averaged square end-to-end distance R^2 of the polyelectrolyte chain, as obtained by a mean-square of the different configurations, is plotted as a function of reduced Coulomb coupling λ_B / σ in Fig. 2. Here we can confirm the collapse scenario found in other simulations[24–26] and analytical treatments.[48] Starting with a swollen chain at zero Bjerrum length λ_B its configuration first stretches with increasing λ_B reaching a maximally stretched state near $\lambda_B / \sigma = 1$ while upon further increase of λ_B the chain recollapses due to the attraction induced by the counterions. For zero Bjerrum length, there are no charges in the system and everything is governed by excluded volume; hence the chain behaves like a polymer coil with end-end distance $R \sim N^{0.588}$. For increasing λ_B / σ, the monomer charges along the polyelectrolyte repel each other since the counterion screening is not very efficient. This leads to a stretched configuration. When the Bjerrum length is of the order of the monomer diameter σ, the chain is maximally stretched. We note that although in our tethered bead model the bond length may vary between σ and 1.5σ, it turns out to

be very stable under variation of the Coulomb interaction. For all the range of λ_B studied the bond length measures $(1.3 \pm 0.05)\sigma$—see also numbers given in the following for the contour length.

As λ_B is increased further, the counterions start to condensate near the polyelectrolyte chain. Then, the charges are effectively neutralized, and attractive polarization fluctuations respectively, correlations induce a chain collapse such that the polyelectrolyte retains a coil-like shape. For large λ_B this counterion induced collapsed state of the chain is generally found to be more compact than the swollen chain at zero Bjerrum length. In the range of λ_B values treated here, this effect is not yet seen.

We now add neutral tail monomers to the charged counterions to form model ionic surfactant molecules ($n = 5, 10$). The results are also shown in Fig. 2. While the addition of a neutral surfactant tail does not affect much the initial stretching in the range $0 < \lambda_B / \sigma < 1$, the subsequent collapse is strongly reduced. The longer the surfactant tail, the stronger the effect of stretching. Even in the regime where the counterionic surfactants condense near the polyelectrolyte chain the configuration remains stretched. This effect is due to the excluded volume interaction of the neutral tails and is analogous to the stretching of densely grafted comb polymers.[49] Consequently the Coulomb coupling where R gets maximal is shifted toward much larger values. This is strongly pronounced for long tails ($n = 10$) where the shift is about a factor of 4.

Snapshots of typical configurations of the complex are summarized in Figs. 3 and 4. The particle coordinates are projected onto a plane containing the end-to-end distance vector. Clearly a bottle-brush architecture due to strongly adsorbed surfactant heads is visible. The nonmonotonicity of R as a function of λ_B / σ can also be seen from the snapshots.

To gain more insight about the structure of the complex we have measured the cross pair correlation $g(r)$ for the polyelectrolyte monomers and the tail end monomers of the surfactant. Here r is the minimal distance from an outermost tail molecule to any polyelectrolyte monomer. The results shown in Fig. 5 are compatible with a bottle brush structure for the polyelectrolyte surfactant complex: The tail end monomers are found most probably at distance $r = 5\sigma$ and $r = 10\sigma$ from the polyelectrolyte chain when the surfactant molecules have $n = 5$ and $n = 10$ monomers. Another quantity of interest is the contour length L of the polyelectrolyte given by the sum of the bond lengths. Our observation is that this quantity is very stable under all changes of the parameters varied in our simulation. Increasing the Bjerrum length in the range $\lambda_B = 0 - 8\sigma$ we find a corresponding increase from $L = 39.9\sigma$ to $L = 41.7\sigma$, a change that is within the statistical uncertainty. This is also the reason why measuring the persistence length L_p does not give additional information as for a worm-like chain it is related to the end-end distance R and the contour length L by[50]

$$R^2 = 2LL_p - 2L_p^2 (1 - \exp(-L/L_p)). \tag{4}$$
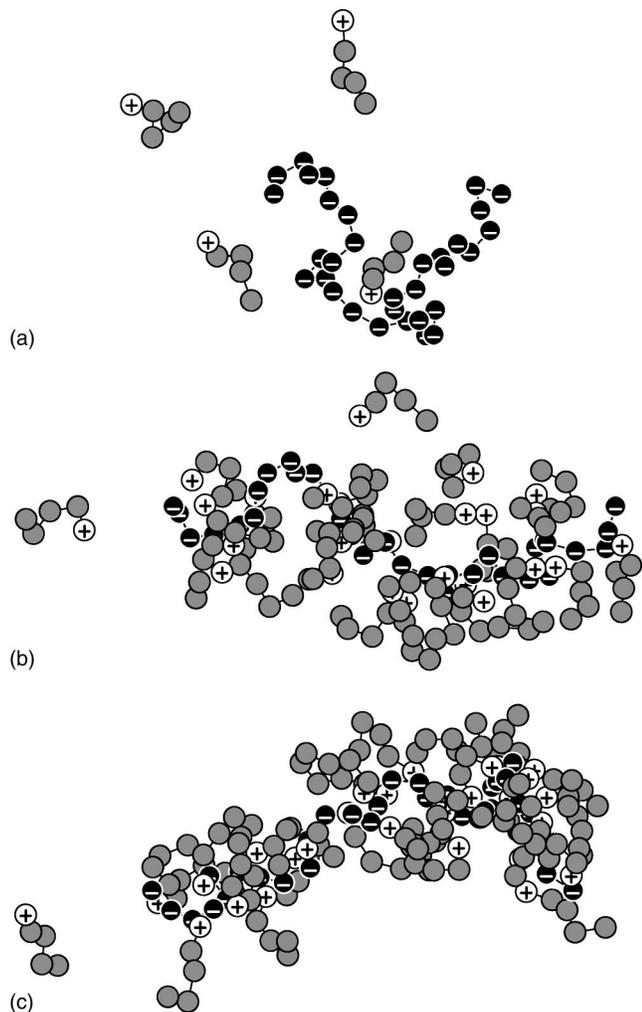
FIG. 3. Polyelectrolyte (PE)–surfactant configurations for a 5-monomer surfactant and a 32-monomer PE in the salt free situation at (a) $\lambda_B = 0$, (b) $\lambda_B = 4\sigma$, (c) $\lambda_B = 8\sigma$. Surfactant molecules are shown only if the distance of their charged bead to the PE chain is less than 8σ.

B. Influence of added salt

The influence of added salt concentration c_s on the end-to-end distance R is shown in Fig. 6. The surfactant molecules in the complex are replaced in favor of salt ions. This is driven by entropy of mixing and corresponds to a chemical equilibrium. The replacement is therefore increasing with increasing salt concentration. This destroys the structure of the complex as seen from the reduction in the end-to-end distance of the polyelectrolyte. When the system is flooded with salt, almost all adsorbed ionic surfactants are replaced by counterions and form Bjerrum pairs with the salt co-ions in the solution. We remark that there is a fundamental difference between a salt-free complex and the situation of added salt in the limit of very small polyelectrolyte concentration: in the former case the complex will dissolve toward a stretched polyelectrolyte chain with dissolved ionic surfactant molecules experiencing their translational entropy while at finite salt concentration the structure of the complex will stay stable. For the $n = 1$ reference system with simple counterions the influence of salt is minimal, the deviations seen in our simulation remain within the statistical uncertainty. In all
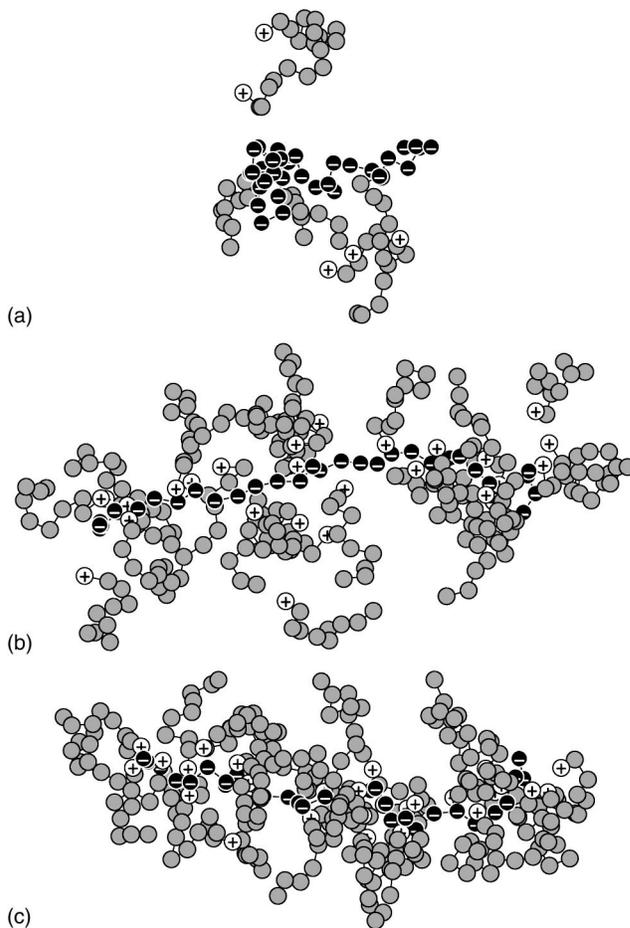
FIG. 4. Polyelectrolyte (PE)–surfactant configurations for a 10-monomer surfactant and a 32-monomer PE in the salt free situation at (a) $\lambda_B = 0$, (b) $\lambda_B = 4\sigma$, (c) $\lambda_B = 8\sigma$. Surfactant molecules are shown only if the distance of their charged bead to the PE chain is less than 8σ.

cases there was no significant change of the contour length L with salt concentration.

Simulation snapshots for the situation with added salt are presented in Figs. 7 and 8. Clearly the reduction of the stretching due to replacement of salt counterions along the polyelectrolyte chain can be seen.
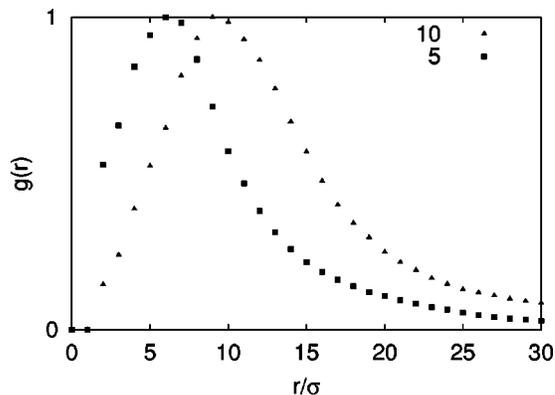
FIG. 5. The pair correlation function $g(r)$ for pairs of a polyelectrolyte monomer and a surfactant tail monomer at Bjerrum length $\lambda_B = 8\sigma$. The functions are scaled to a maximum value of 1. The maximal number of tail ends is found at $r = 6\sigma$ from the polyelectrolyte backbone in the case of $n = 5$ monomer surfactants. For $n = 10$ this most probable distance is $r = 9\sigma$.
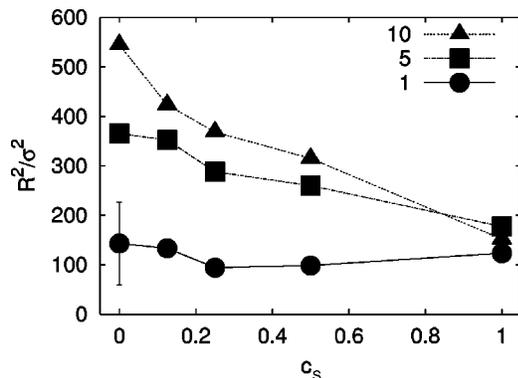
FIG. 6. The mean squared end-to-end distance R^2 for Bjerrum length $\lambda_B = 8\sigma$ as a function of the relative salt concentration c_s for $n=1,5$ and $n=10$ monomer surfactants. The statistical uncertainty is indicated by an error bar.

V. CONCLUSIONS

In conclusion, we have studied the complex formation between a single polyelectrolyte and oppositely charged ionic surfactants together with added salt. The end-to-end distance of the polyelectrolyte in the resulting bottle brush complexes exhibits a nonmonotonic variation with increasing Coulomb interaction strength. This reflects the known collapse as induced by counterions. The excluded volume of the flexible chain, however, efficiently blocks the collapse. Additional salt counterions may replace adsorbed ionic surfactant molecules and thus reduce the chain elongation. Our

FIG. 8. Polyelectrolyte (PE)–surfactant configurations for a 10-monomer surfactant and a 32-monomer PE for relative salt concentrations (a) $c_s = 0.25$ and (b) $c_s = 1$, both at $\lambda_B = 8\sigma$. Surfactant molecules and salt ions are shown only if the distance of their charged bead to the PE chain is less than 8σ.
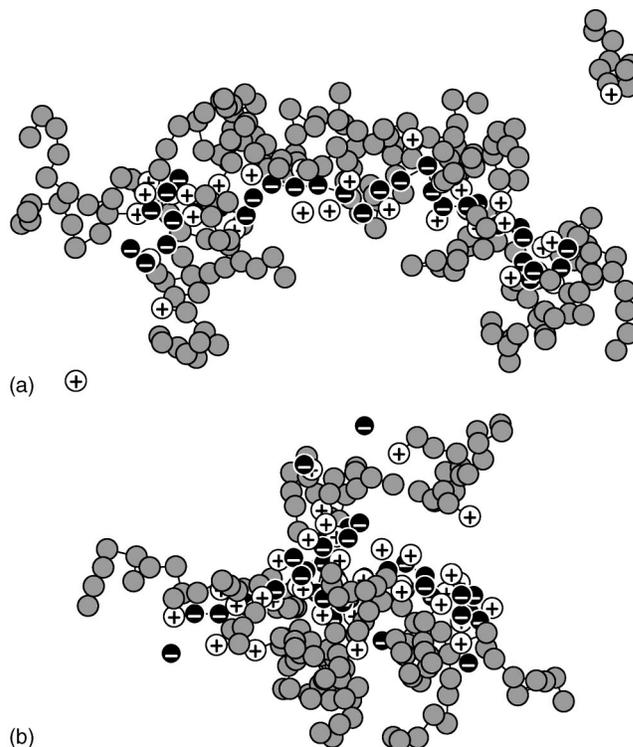
FIG. 7. Polyelectrolyte (PE)–surfactant configurations for a 5-monomer surfactant and a 32-monomer PE for relative salt concentrations (a) $c_s = 0.25$ and (b) $c_s = 1$, both at $\lambda_B = 8\sigma$. Surfactant molecules and salt ions are shown only if the distance of their charged bead to the PE chain is less than 8σ.

results can in principle by verified in experiments by systematically varying the surfactant tail length (of e.g., hydrocarbon chains) and the surfactant/polyelectrolyte charge and/or the dielectric permittivity of the solvent.

Our model can be extended into several directions which will be interesting in future studies. First it would be interesting to study high valency salt ions resulting in high Coulomb coupling. Then overcharging effects of the polyelectrolyte are expected.[51] Second, the model can be made more realistic by taking empirical force fields and explicit solvent molecules.[52] An explicit solvent, however, will slow down the simulation time significantly.[53] Since the interaction is dominated by the Coulomb forces, we expect that at least qualitatively the complex formation will exhibit similar trends as a function of Coulomb coupling and salt concentration.

Another challenging extension of our model is to high surfactant and/or finite polyelectrolyte concentrations. If the concentration of ionic surfactant (together with counterions) exceeds the critical micelle concentration, a single polyelectrolyte chain may self-assemble with the charged spherical micelles into complexes. For a single micelle modeled as a charged sphere, many recent studies have revealed different topologies of the defect depending on the chain stiffness.[54–69] As known from neutral systems, necklace formation along the polyelectrolyte is also conceivable. On the other hand, for high polyelectrolyte concentrations, a self-assembly into lamellar sheets of alternating charged sheets of polyelectrolytes and surfactants[70] is possible and it would be

very interesting to explore details of this self-aggregation phenomenon by computer simulation.

ACKNOWLEDGMENTS

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