Effect of monovalent salt on the conformation of polyelectrolyte-surfactant complexes

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We study the conformation of polyelectrolyte-surfactant complexes in the presence of monovalent salt. A simple model for the formation of these structures is presented in the framework of the Debye-Hückel-Bjerrum-Manning and Flory theories, with the hydrophobic interactions between the hydrocarbon tails of surfactant molecules treated in the spirit of van der Waals theory as an effective attraction. The extension of the polyelectrolyte-surfactant complexes is analyzed as a function of the salt concentration and a discrete conformational transition between a compact globule and an elongated coil is found, in agreement with experimental results for the unfolding transition of a DNA-cationic surfactant complex.

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I. INTRODUCTION

Solutions containing polyelectrolytes and oppositely charged ionic surfactant molecules have received a lot of attention in recent years. In addition to the wide technological and biomedical applications associated with these systems [1–3], from a theoretical perspective the presence of very intricate microscopic interactions, driven mostly by electrostatic and hydrophobic forces, make a precise molecular description a challenging task [4–8].

Recently, we have studied the conformation of a flexible polyelectrolyte in the presence of cationic surfactant molecules [9]. A simple model based on the Debye-Hückel and Flory ideas for the formation of the polyelectrolyte-surfactant complex in a *salt-free* solution was introduced. The distribution of the complexes has been evaluated, taking into account their polydispersity explicitly as well as the hydrophobic interaction between the hydrocarbon tails of the surfactant molecules that are condensed on the charged polyelectrolyte monomers. As a result, a discrete conformational transition between an elongated coil and a compact globule was found, as a function of the surfactant concentration, in qualitative agreement with the experimental observations [10]. The transition was found for a very low surfactant concentration, below the critical micelle concentration (cmc), which is defined as the concentration at which the surfactant molecules start to self-aggregate into structures called micelles.

With the addition of simple salts, the cmc starts to decrease, since the electrostatic repulsion between the positively charged hydrophilic head groups of surfactant molecules is reduced by the presence of the negatively charged ions from salt. Hence, the micellization process is facilitated and occurs for a lower surfactant concentration compared to the salt-free case. For cetyltrimethylammonium bromide (CTAB), for instance, the cmc is approximately 10^{-3} M for a solution with no salt, decreasing to approximately 10^{-5} M with the addition of 0.1 M of KBr salt [11]. Therefore, in order to characterize the structure of the polyelectrolyte-surfactant complexes in the presence of salt we have to consider the micelle formation. Unfortunately, the physicochemical description of surfactant self-assembly is very complicated, mainly due to the diversity of shapes and sizes presented by the micelles, which includes spheres, globules, cylinders, and spherical bilayer vesicles [12–14]. Also, a sphere-rod transition of the CTAB micelles with the increase of salt concentration is expected [15,16]. Although a lot of experimental effort [17–20] has been made in order to understand the different structures of the polyelectrolyte-surfactant complexes, a systematic theory that explains all the microscopic interactions in such a system is still lacking.

In this paper, we extend our previous model for the polyelectrolyte-surfactant complex formation [9] taking into account the presence of a simple monovalent salt. The interactions between the chemical species in the polyelectrolyte-surfactant complexes are treated explicitly. Briefly stated, we study the electrostatic interaction in the framework of the Debye-Hückel-Bjerrum-Manning theory [21–24], including the salt particles into the model, along with the Flory elasticity theory [25,26] for the elastic degrees of freedom. The hydrophobic interactions between the hydrocarbon tails of the surfactant molecules are explicitly taken into account as an effective short-range attraction, in the spirit of the van der Waals theory [27]. Differently from Ref. [9], we consider the presence of free micelles in the bulk solution as a new chemical species, since the surfactant concentrations we are using are larger than the cmc in salty solutions. Using the experimental estimates of CTAB cmc [11] we propose a simple free energy that describes the presence of these micelles. As a result, we find a discrete conformational transition for the polyelectrolyte-surfactant complexes as a function of the salt concentration. The paper is organized as follows: in Sec. II, we present the model system and the theoretical approach used to obtain the total free energy for a solution containing free micelles, polyelectrolyte-surfactant complexes, and salt particles. Section III discusses the results and Sec. IV presents the conclusions.

II. MODEL SYSTEMS

In our model we have essentially the same chemical species used in our previous work: N_p flexible polyelectrolytes

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with charge $-Zq$, Z counterions of charge $+q$, in order to maintain the electroneutrality, and oppositely charged surfactant molecules. In an aqueous solution, these surfactant molecules become ionized producing a flexible chain, composed of one hydrophilic head group of charge $+q$ and a hydrophobic tail with z_a neutral monomers, along with a free ion of charge $-q$, or coion, produced to maintain the electroneutrality. Differently from Ref. [9], in this work we include a monovalent salt in the solution. Therefore, since it is expected that cmc starts to decrease with the addition of salt, the approximation of a solution with no free micelles used previously is not justified. We also have to consider the presence of charged micelles in the bulk solution, with no polyelectrolytes, along with the polyelectrolyte-surfactant complexes introduced in Ref. [9]. For simplicity, we consider all monomeric constituents in the solution as hard spheres with the same diameter $\sigma=3$ Å.

A. Free energy of the micelles

In this section, we discuss the presence of cationic surfactant aggregates, since it is expected the appearance of such structures whole over the bulk solution with the addition of salt. We consider a solution with no polyelectrolytes, containing a given concentration of surfactant and monovalent salt, dispersed in a solvent represented by a dielectric constant D. Although the size and shape of the micelles show a dependence on temperature and salt concentration, for simplicity, we shall consider that all micelles have an average the same number g of surfactant molecules and radius R_g. We do not consider the possibility of having micelles with different sizes for a given salt concentration. This is equivalent to the optimum micelle size approach introduced by Rao and Ruckenstein [16], where only the contribution of the most populous micelle size is considered in the calculation of the properties of micellar solutions. Once the micelles are formed, the positive charges on the polar head groups will attract a given number of negatively charged ions of salt. Although this number may be different for each micelle, in this work we neglect polydispersity and consider that, on average, all micelles of size g have the same number n_g of associated negative ions, with the corresponding associated fraction given by $m_g=n_g/g$, for a given salt concentration. The number of unassociated surfactant molecules, free counterions, co-ions, and micelles in the solution are $N_{a,f}$, N_+, N_-, and N_g, respectively. Therefore, the number densities can be written as

$$\rho_+ = \rho_s,$$

$$\rho_- = \rho_s + \rho_a - g m_g \rho_g,$$

$$\rho_{a,f} = \rho_a - g\rho_g,$$

$$\rho_g = \frac{f}{g}\rho_a, \tag{1}$$

where f is the fraction of surfactant molecules that form micelles, ρ_s is the salt density, and ρ_a is the surfactant density.

With all these definitions, the Helmholtz free energy that describes the presence of free micelles can be written as a sum of different contributions,

$$F_m = F_m^{\mathrm{el}} + F_m^{\mathrm{DH}} + F_m^{\mathrm{CS}} + F_m^{\mathrm{id}} + F_m^{\mathrm{int}}, \tag{2}$$

where F_m^{el} and F_m^{DH} are the two types of electrostatic contributions, F_m^{CS} is the excluded volume free energy, F_m^{id} is the ideal gas term, and F_m^{int} is the free energy corresponding to the internal partition function of the micelles.

The electrostatic contributions are represented by the free energy corresponding to the interaction between the spherical micelles and the free ions in the solution [27],

$$\beta F_m^{\mathrm{el}} = -\frac{1}{2} g^2 N_g \lambda_B (1-m_g)^2 \frac{\kappa}{1+\kappa R_g}, \tag{3}$$

along with the interaction between the unassociated ions, represented by the Debye-Hückel approximation [21,24,28,29],

$$\beta F_m^{\mathrm{DH}} = -\frac{V}{4\pi\sigma^3}\left[\ln(1+\kappa\sigma) - \kappa\sigma + \frac{(\kappa\sigma)^2}{2}\right]. \tag{4}$$

Here, $\kappa=\sqrt{4\pi\lambda_B(\rho_+ + \rho_- + \rho_{a,f})}$ is the inverse Debye screening length and $\lambda_B=\beta q^2/D=7.2$ Å is the Bjerrum length for water.

For the excluded volume interaction, we use the Carnahan-Starling theory [30], with the corresponding free energy represented by

$$\beta F_m^{\mathrm{CS}} = (N_+ + N_- + N_{a,f} + N_g) y \frac{(4-3y)}{(1-y)^2}, \tag{5}$$

where

$$y = \frac{\pi}{6}\bar{\sigma}^3(\rho_+ + \rho_- + \rho_{a,f} + \rho_g). \tag{6}$$

The characteristic length $\bar{\sigma}$ is given by

$$\bar{\sigma} = \frac{\rho_+\sigma + \rho_-\sigma + \rho_{a,f}\sigma_a + \rho_g(2R_g)}{\rho_+ + \rho_- + \rho_{a,f} + \rho_g}, \tag{7}$$

where σ_a is the diameter of a sphere with the same volume of a surfactant molecule,

$$\sigma_a = \sigma(1+z_a)^{1/3}. \tag{8}$$

The ideal gas free energy is written as usual, just adding the entropic contributions of different species,

$$\beta F_m^{\mathrm{id}} = N_+ \ln(\rho_+\Lambda^3) - N_+ + N_- \ln(\rho_-\Lambda^3) - N_- + N_{a,f}\ln(\rho_{a,f}\Lambda^3) - N_{a,f} + N_g \ln(\rho_g\Lambda^3) - N_g, \tag{9}$$

where $\Lambda=h/\sqrt{2\pi m k_B T}$ is the mean thermal wavelength. For simplicity, for the structureless counterions and coions, unassociated surfactant molecules, and free micelles we take $\Lambda=\sigma$.

For the free energy corresponding to the internal partition function of micelle formation, we follow the procedure used in Ref. [9]. Briefly stated, the electrostatic interaction is divided in two terms: a repulsive part, due to the net charge on the surface of the spherical micelles, and an attractive term,

produced by the association between the negative ions in the solution and the positive charges on the micelles. In addition, we also have to include the hydrophobic interaction between the neutral monomers on the surfactant tails, using the van der Waals theory introduced in Ref. [9]. In this approach, the hydrophobic effect is represented by an effective attraction between the hydrocarbon monomers, which we model through a square-well potential,

$$u_{\mathrm{hy}} = \begin{cases} \infty, & r < \sigma_{\mathrm{eff}} \\ -\varepsilon_0, & \sigma_{\mathrm{eff}} \leqslant r < 2\sigma_{\mathrm{eff}} \\ 0, & r \geqslant 2\sigma_{\mathrm{eff}}, \end{cases} \tag{10}$$

where $\sigma_{\mathrm{eff}}=z_a^{1/3}\sigma$ represents the effective diameter of a sphere formed exclusively by the z_a monomers of the surfactant tail, and ε_0 represents the intensity of the hydrophobic interaction. We use $z_a=16$, corresponding to the CTAB surfactant [10]. Therefore, the free energy corresponding to the internal partition function of the micelles can be written as [9]

$$\beta F_m^{\mathrm{int}} = gN_g m_g \ln m_g + gN_g(1-m_g)\ln(1-m_g) - gN_g m_g \ln \frac{\zeta_2}{\Lambda^3} + g^2 N_g \frac{\lambda_B}{2R_g}(1-m_g)^2 - \frac{14}{3}\pi\beta\varepsilon_0 g^2 N_g \frac{z_a\sigma^3}{V_g}, \tag{11}$$

where $V_g=4\pi R_g^3/3$ is the volume occupied by the micelle. The first two terms are the entropic contributions, while the third one is the attractive part due to the dipole formation, with the association constant ζ_2 written as [22,24]

$$\zeta_2 = \frac{2\pi\sigma^3}{3t^3}\left[\mathrm{Ei}\left(\frac{1}{t}\right) - \mathrm{Ei}(2) + e^2\right] - \frac{2\pi\sigma^3}{3}e^{1/t}\times\left[2+\frac{1}{t}+\frac{1}{t^2}\right], \tag{12}$$

where $t=\sigma/\lambda_B$, which is valid for $t<0.5$, such that $\zeta_2=0$ at high temperatures. The last two terms of Eq. (11) are the repulsive and hydrophobic interactions, respectively.

B. Free energy of the complexes

Due to the strong electrostatic interactions between the Z charged groups along the polyelectrolytes, free counterions, and the hydrophilic head groups of surfactant molecules we must expect a new type of complex, along with the free micelles discussed in the preceding section. This new complex is composed by one polyelectrolyte chain, n_c counterions, and n_a amphiphilic molecules, in the same spirit of our previous work [9]. Differently from that study, in this work, we simplify the model considering that all complexes have, on average, the same number of associated counterions and surfactant molecules. We do not calculate the complex distribution, since most of the complexes have a typical number of associated counterions and surfactant molecules, as shown in Fig. 1 of Ref. [9]. Hence, we define the fraction of associated counterions and surfactants as $m_c=n_c/Z$ and $m_a=n_a/Z$, respectively. It should be noted that in Ref. [9] the number of complexes was identified by N_{ij}, where i and j were the number of condensed counterions and surfactants, respectively, such that the density of complexes was $\rho_{ij}=N_{ij}/V$. In this study, these quantities are replaced by n_c and n_a, respectively. The number density of the polyions is ρ_p, and the surfactant and monovalent salt are identified by ρ_a and ρ_s, respectively. Therefore, if $Z\rho_p$ is the density of monomers, Eq. (1) must be rewritten as follows:

$$\rho_+ = \rho_s + Z\rho_p - m_c Z\rho_p,$$

$$\rho_- = \rho_s + \rho_a - g m_g \rho_g,$$

$$\rho_{a,f} = \rho_a - g\rho_g - m_a Z\rho_p,$$

$$\rho_g = \frac{f}{g}\rho_a. \tag{13}$$

The Helmholtz free energy for the whole system is constructed adding to F_m, evaluated in Sec. II A, the terms corresponding to the interactions originated by the presence of the polyelectrolyte chains,

$$F = F_m + F_p^{\mathrm{d}} + F_p^{\mathrm{hc}} + F_p^{\mathrm{DH}} + F_p^{\mathrm{mix}}, \tag{14}$$

where F_p^{d} is the deformation free energy, F_p^{hc} is the excluded volume contribution, F_p^{DH} is the Debye-Hückel approximation for the electrostatic contribution, and F_p^{mix} is the entropic free energy of the mixture. These free energies are calculated with the same procedure of Ref. [9].

The elastic deformation free energy is given the Flory-de Gennes theory [25,26],

$$\beta F_p^{\mathrm{d}} = N_p\left(\frac{3}{2}(\alpha^2-1) - 3\ln\alpha\right), \tag{15}$$

where $\alpha=R/R_0$ is the extension factor of the polyelectrolyte chain, in a complex with the extension

$$R = \sigma(Z-1)^{\gamma}, \tag{16}$$

measured relative to the nonstrained Gaussian extension $R_0=\sigma(Z-1)^{1/2}$. Hence, the exponent γ in Eq. (16) is a measure of the deviation from the Gaussian limit.

The excluded volume interaction inside of the complex is expressed by

$$\beta F_p^{\mathrm{hc}} = \frac{2\pi\sigma^3}{3}(Z+n_c+n_a)^2\frac{N_p}{V_R} - n_a z_a N_p \ln\left(1-\frac{2\pi\sigma^3}{3}\frac{n_a z_a}{V_R}\right), \tag{17}$$

where $V_R=4\pi R^3/3$ is the volume occupied by the complex. The first term corresponds to the virial expansion, due to the interaction between the Z polyelectrolyte monomers and the condensed counterions and surfactant molecules. The second term is a free-volume approximation for the interaction between the neutral tail monomers of the condensed surfactant molecules.

The electrostatic interaction between the charges in the complexes and the free ions is calculated in the framework of the Debye-Hückel-Bjerrum [21,22] and Manning theories [23],

$$\beta F_p^{\mathrm{DH}} = \lambda_B N_p p^2 \mathcal{I}. \tag{18}$$

Here, $p=-1+m_c+m_a$ is the net valence for each monomeric site along the polyelectrolyte chain, and

$$\mathcal{I} \equiv \int_0^Z (Z-x)\frac{e^{-\kappa r(x)}-1}{r(x)}dx, \tag{19}$$

where $r(x)=\sigma x^{\gamma}$ and κ is the inverse Debye screening length.

For the entropic part we have to consider the ideal contribution of the complexes, along with the internal partition function for the formation of these entities [9]. To this end, we have to model the hydrophobic interaction between the neutral tail monomers on the condensed surfactant molecules. As shown in Sec. II A, the hydrophobic interaction in the free micelles is represented by a square-well potential, Eq. (10), with the attractive strength represented by ε_0. For the complexes with the polyelectrolytes, we use a different attractive strength ε, employing the same definition of Eq. (10). Therefore, the entropic free energy is written as [9]

$$\beta F_p^{\mathrm{mix}} = N_p \ln(\rho_p \Lambda^3) - N_p - N_p(n_c+n_a)\ln\frac{\zeta_2}{\Lambda^3} + ZN_p(m_c \ln m_c + m_a \ln m_a - p\ln|p|) + N_p\frac{\lambda_B}{\sigma}p^2\sum_{n=1}^{Z-1}\frac{Z-n}{n^{\gamma}} - \frac{14\pi}{3}\beta\varepsilon n_a^2 N_p \frac{z_a\sigma^3}{V_R}. \tag{20}$$

The corresponding entropic contributions from the other chemical species (free micelles and free particles) are included in Eqs. (9) and (11).

In principle, once we have the total Helmholtz free energy, Eq. (14), the thermodynamics of the system is determined by the minimization of this equation with respect to the five parameters that determine the structure and conformation of the complexes, γ, m_c, m_a, f, and m_g, respectively.

III. RESULTS AND DISCUSSION

We start considering the presence of micelles in the bulk solution, assuming that the cmc location is not affected by the presence of the polyelectrolytes. This assumption is justified for the low polylectrolyte concentrations we are analyzing, since it corresponds to the individual DNA's behavior reported in Ref. [17]. In Table I we show the experimental values of CTAB cmc [11] and the number g of surfactant molecules in each micelle [31–33] as a function of salt concentration. To estimate the size of the micelles, we consider a close-packed sphere of radius

$$R_g = \left(\frac{3}{4\pi}g v_a\right)^{1/3}, \tag{21}$$

composed by g surfactant molecules, each one occupying a volume v_a given by

$$v_a = \frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3(1+z_a). \tag{22}$$

For $z_a=16$ and $\sigma=3$ Å, the values we are assuming for the CTAB surfactant, Eqs. (21) and (22), will produce a radius of $R_g \approx 17.35$ Å for a solution with no salt, as shown in Table I. This value is lower than the experimental estimate for spherical micelles of CTAB with an aggregation number equal to 91, which have a typical hydrodynamic radius of 26 Å at high temperatures [31,32,34]. With the addition of salt this radius increases, as shown in Table I.

TABLE I. Critical micelle concentration of CTAB (ρ_a) [11] and micelle aggregation number (g) [31–33], as a function of KBr salt concentration (ρ_s). The radius of a spherical micelle of CTAB (R_g) is calculated through Eqs. (21) and (22).

ρ_s (M)	ρ_a ($\times 10^{-3}$ M)	g	R_g (Å)
0	0.955	91	17.35
0.0034	0.363	97.2	17.73
0.0102	0.155	109.6	18.46
0.0182	0.102	124.19	19.24
0.0323	0.0687	149.91	20.49
0.0562	0.047	193.5	22.31
0.1	0.0316	301.91	25.87
0.197	0.02	1932.3	48.04
0.316	0.0145	3590.64	59.06

In order to describe the presence of free micelles we have to fix the hydrophobic strength ε_0 introduced in Eq. (10). To this end we use the values listed in Table I and minimize Eq. (2) with respect to f and m_g, for different values of ε_0. The results are shown in Fig. 1 for different salt concentrations. Clearly, f and m_g show an abrupt change at approximately $\varepsilon_0=(0.66\pm0.01)k_BT$, independently of the salt concentration, which we identify in our model as the location where the micellization process starts, for each one of the salt concentrations under consideration. Experimentally, the same procedure is taken when the cmc is determined by observing sudden changes in physical properties, such as air-water solution surface tension, viscosity, and electrical conductivity [11,35,36].

Next, we consider the formation of the complexes, composed by one polyelectrolyte and a given fraction of surfactant and counterions, as a function of the salt concentration, given by the total Helmholtz free energy, Eq. (14). The density of monomers was fixed at $Z\rho_p=0.6$ μM, with $Z=128$, and for the surfactant concentrations we have chosen $\rho_a=1\times10^{-4}$ M and 0.137 M, the same concentrations used in Ref. [17] for T4DNA complexed with CTAB. For the hydrophobic strength ε, used in Eq. (20), we have chosen a value such that the coil-globule transition occurs at the same salt concentration ρ_s^c as observed experimentally by Mel'nikov *et al.* [17]. To this end, for the surfactant concentrations above, we have used $\varepsilon=(6.0\pm0.1)k_BT$. It should be noted that we have used $\varepsilon=3.6k_BT$ in our previous work [9]; that is, the hydrophobic strength parameter is not universal in our model.

The total free energy, Eq. (14), is a function of the number of associated particles (counterions and surfactant molecules), extension of the chain, and micellization parameters, $F=F(m_c,m_a,\gamma,f,m_g)$. Therefore, in principle, we have to minimize this equation with respect to all of these variables. However, since this work considers a very diluted solution of

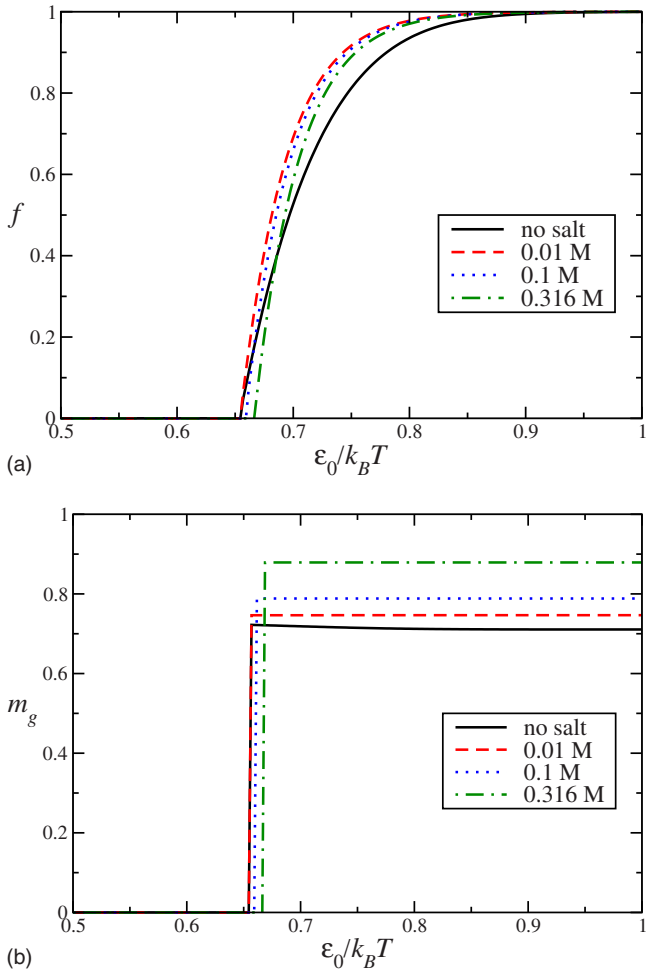

FIG. 1. (Color online) (a) The fraction f of surfactant molecules that forms micelles and (b) the fraction m_g of condensed negative ions, as a function of the hydrophobic strength ε_0. For each salt concentration we have used the following experimental estimate for cmc [11]: $\log_{10}\rho_a=-3.02$ (no salt), $\log_{10}\rho_a=-3.81$ (0.01 M), $\log_{10}\rho_a=-4.50$ (0.1 M), and $\log_{10}\rho_a=-4.84$ (0.316 M).

polyelectrolytes, we use an approximation where the micelle formation in the solution is not affected by the presence of the polyelectrolytes. Hence, we minimize the free energy of the micellization process, Eq. (2), in order to find f and m_g for a given surfactant and salt concentrations, with the attractive hydrophobic strength fixed at $\varepsilon_0=(0.66\pm0.01)k_BT$, as discussed previously.

Once these values are obtained, the thermodynamics of the complexes is determined by the minimization of the complete free energy, Eq. (14), with respect to the condensed fractions of particles m_c and m_a, for counterions and surfactants, respectively, and the exponent for the extension of the complexes, γ. The results are shown in Fig. 2. For the surfactant concentrations used in this work, in the absence of salt, we have shown previously that the polyelectrolyte-surfactant complexes are found in a more compact configuration, with the exponent γ closer to the Gaussian state value 0.5 [9]. With the addition of monovalent salt in the solution, we expect that the cmc will start to decrease, as shown in Table I. Even for low salt concentrations, we have to consider the micelle formation in the solution (e.g., when $\rho_s=0.1$ M the cmc is approximately 3×10^{-5} M). As a result, when salt is added to the solution the surfactants that are condensed on the polyelectrolyte monomers are replaced by the counterions from the salt, as shown in Fig. 2. While most of the surfactant molecules move to the solution in order to self-aggregate into charged micelles, such that the fraction of condensed surfactant m_a decreases, the fraction of condensed counterions m_c increases continuously. However, at a certain critical salt concentration ρ_s^c a discontinuous transition in the condensed fractions is observed. For $\rho_a=1\times10^{-4}$ M the transition occurs at $\rho_s^c\approx0.44$ M, while for $\rho_a=0.137$ M it happens at $\rho_s^c\approx0.34$ M. Above these salt concentrations, the complexes are composed mostly by counterions, since the fraction of condensed surfactant becomes negligible, as shown in Fig. 2.

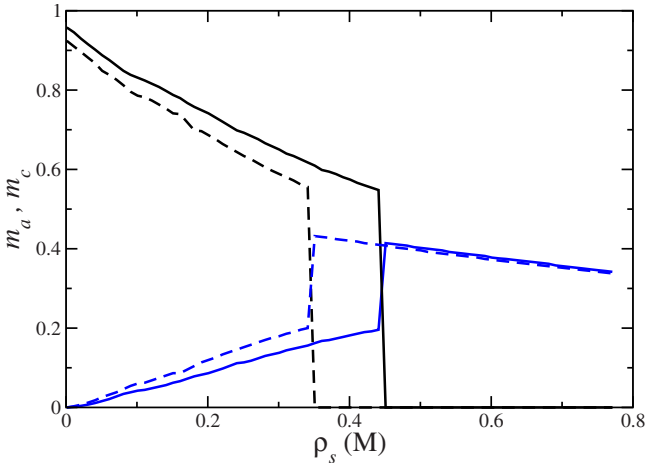

FIG. 2. (Color online) The fraction m_a of condensed surfactants (black line) and the fraction m_c of condensed counterions (blue line), as a function of the salt concentration, for $\rho_a=1\times10^{-4}$ M (solid line) and 0.137 M (dashed line). The number of polyelectrolyte monomers is $Z=128$.

In order to better understand this discrete transition, we calculate the extension of the complexes through the end-to-end distance, Eq. (16), or, equivalently, by the extension exponent γ, as a function of the salt concentration. The results are shown in Fig. 3. For a *low* salt concentration, the complexes are collapsed, mainly due to the hydrophobic interaction between the neutral monomers of the surfactant molecules, which favors the accumulation of these molecules on the polyelectrolyte charged monomers. The charge of the polyelectrolyte is strongly renormalized and the extension exponent is close to the nonstrained Gaussian state $\gamma=0.5$. On the other hand, for a *high* salt concentration, the complexes are found in a more extended conformation, since now the charge renormalization produced by the salt counterions is small and the hydrophobic effect disappears completely in the complexes. Between these two limits, at a salt concentration near to ρ_s^c, the collapsed and extended conformations coexist, as shown in Fig. 3. The same coexistence was observed experimentally by Mel'nikov *et al.* [17] for T4DNA complexed with CTAB.

It is interesting to see that if we remove the hydrophobic interaction between the hydrocarbon tails of the surfactant

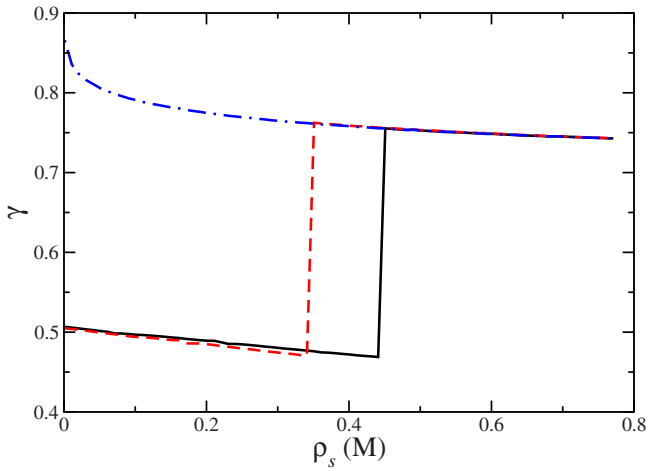

FIG. 3. (Color online) The end-to-end exponent of the complexes as a function of the salt concentration. The surfactant concentrations are the same as in Fig. 2. We also include the resulting extension exponent when $\varepsilon=0$ (dot-dashed line) and $\rho_a=1\times10^{-4}$ M.

molecules in our model, the discrete conformational transition disappears completely. In fact, for $\varepsilon=0$ the complexes are in a more extended configuration, as shown in Fig. 3. The addition of monovalent salt is followed by a small charge renormalization of the polyelectrolytes, and the complexes become less extended continuously. These findings confirm our previous observation that the conformation of the complexes is not only driven by the electrostatic interactions, but also is strongly dependent on the hydrophobic interactions between the surfactant molecules [9].

IV. CONCLUSIONS

Using the Debye-Hückel-Bjerrum-Manning and Flory theories, we have studied the effect of monovalent salt on the conformation of polyelectrolyte-surfactant complexes. We have proposed a simple model for the hydrophobic interactions between the hydrocarbon tails of surfactant molecules. The extension of the polyelectrolyte-surfactant complex has been calculated as a function of the salt concentration for two different surfactant concentrations. As a result, a discontinuous conformational transition from a collapsed state to an extended one was found at some critical salt concentration. These findings are in agreement with the experimental estimate for the unfolding transition of the DNA-cationic surfactant complex [17].

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