# Flexible polyelectrolyte conformation in the presence of oppositely charged surfactants

P. S. Kuhn and A. Diehl*
*Departamento de Física, Instituto de Física e Matemática, Universidade Federal de Pelotas, Caixa Postal 354, CEP 96010-900, Pelotas, RS, Brazil*

(Received 13 June 2007; revised manuscript received 10 September 2007; published 26 October 2007)

Conformational behavior of flexible polyelectrolytes in the presence of monovalent cationic surfactants is examined. A simple model is presented for the formation of polyelectrolyte-surfactant complexes in salt-free solutions in the framework of the Debye-Hückel-Bjerrum-Manning and Flory theories, including explicitly the hydrophobic interactions between the associated surfactant molecules on the polyelectrolyte. The distribution of complexes is calculated as a function of the surfactant concentration and a discrete conformational transition between an elongated coil and a compact globule was found, in agreement with experimental observations.

DOI: 10.1103/PhysRevE.76.041807 PACS number(s): 61.25.Hq, 82.30.Nr, 82.60.Lf

## I. INTRODUCTION

Mixtures of polymers and surfactants are ubiquitous. They are found in many technological applications, such as food industry, production of water-soluble paints and, recently, from a pharmaceutical perspective, in gene therapy, using surfactant molecules to deliver DNA chains into the cells [1]. The problem is particularly fascinating because both the DNA and the cellular membrane are negatively charged and, in principle, must repel each other. In addition, the DNA, a highly charged polyion, in its unpackaged form is a wormlike chain with a persistence length of approximately 500 Å [2]. In the other extreme, when packaged in viral heads or nuclear zone in procaryotic cells, it is highly concentrated, with the helices parallel to each other and separated by roughly 5 Å of water. Therefore, based only on the electrostatic repulsion between the DNA base pairs, is unlikely to find the DNA into the cells.

Complexation of polyelectrolytes and/or surfactant molecules is a very complex process, driven by different types of molecular interactions. Despite a lack of such precise molecular description, some features had emerged from a large number of experimental [3–8] and theoretical [9–16] studies. Whereas undressed DNA is strongly repelled by the negatively charged membrane, complexes consisting of polyelectrolytes and oppositely charged surfactants can approach the cell membrane, mainly due to the DNA charge renormalization produced by the condensed cationic surfactant molecules. Another aspect is the stabilization of the DNA-surfactant complex. For the cationic surfactant cetyltrimethylammonium bromide (CTAB) and DNA, in aqueous solution, for instance, it was found that large DNA chains exhibit a discrete coil-globule conformational transition with the addition of a small quantity of these amphiphiles [3,5]. The molecular description of polyelectrolyte-surfactant interactions involves the combination of both electrostatic attraction, between the positively charged surfactant head groups and the negatively charged DNA phosphate groups, and hydrophobic interactions, between the lilophilic moieties of the surfactant molecules, which favor the accumulation of these molecules. Hence, the resulting compact DNA-surfactant complex could, in principle, be internalized into the cell.

In this paper, we present a simple model for the formation of the polyelectrolyte-surfactant complex in a salt-free solution. The model system uses the Debye-Hückel-Bjerrum-Manning [17–20] ideas for the electrostatic interaction along with the Flory elasticity theory [21,22]. Also, the hydrophobic interactions between the associated cationic surfactant molecules on the polyelectrolyte are explicitly taken into account. These ideas have been used recently for solutions containing rigid and flexible polyelectrolytes, salt and surfactant molecules [9–11]. However, contrary to these previous works, where the one cluster size approximation was used, in this paper we calculate the complex size distribution explicitly. The paper is organized as follows. In Sec. II the model system and the theoretical approach are presented. Section III discusses the results and Sec. IV contains the conclusions.

## II. MODEL AND THEORY

### A. Model

The model system considers a mixture of $N_p$ flexible polyelectrolytes and oppositely charged surfactant molecules in a salt-free solution. The polyelectrolyte chain contains $Z$ uniformly spaced monomers separated by $b$, each of which has an electronic charge $-q$. Due to the macroscopic electroneutrality condition, we have $Z$ counterions of charge $+q$ in the solution. The cationic surfactant molecule in an aqueous solution becomes ionized, producing two different species: a flexible chain, composed of one hydrophilic head group of charge $+q$ and a hydrophobic tail with $z_a$ neutral monomers, and a free ion of charge $-q$, or coion, produced in order to maintain the electroneutrality.

The strong electrostatic interactions between the $Z$ charged groups along the polyelectrolyte, the free counterions, and the hydrophilic head groups of surfactant molecules leads to complex formation. Each complex is composed of one polyelectrolyte chain and a certain quantity of counterions and surfactants. Let us denote by $N_{ij}$ the number of complexes in the solution with $i$ counterions and $j$ surfactants. The corresponding number density of these complexes is

*Corresponding author. diehl@ufpel.edu.br

 

$\rho_{ij}=N_{ij}/V$, where $V$ is the total volume of the system. The number density of polyions is $\rho_p=N_p/V$, while the surfactant concentration is $\rho_a$. The number of unassociated surfactant molecules, free counterions, and coions in the solution are $N_{a,f}$, $N_+$, and $N_-$, respectively. Therefore, if the density of monomers is $Z\rho_p$, then it is possible to express all these number densities by the expressions

$$\rho_{a,f} = \rho_a - \sum_{i,j} j\rho_{ij},$$

$$\rho_+ = Z\rho_p - \sum_{i,j} i\rho_{ij},$$

$$\rho_- = \rho_a, \tag{1}$$

with the constraint

$$\sum_{i,j} \rho_{ij} = \rho_p. \tag{2}$$

Here, the sums run over $i=0,\ldots,Z$ and $j=0,\ldots,Z-i$, since the maximum number of associated particles is $Z$.

The surfactant concentration in this work is lower than the critical micelle concentration (cmc), which for CTAB is approximately 1 mM [23,24]. Therefore, we do not have free micelles in the solution. Also, for simplicity, we consider all monomeric units in the solution having the same diameter $\sigma$ and $b=\sigma$. The solvent that occupies the total volume is represented by a uniform medium of a dielectric constant $D$, and the temperature of the system is $T$.

### B. Helmholtz free energy

In this work we consider a very dilute solution of polyelectrolytes. Therefore, we can neglect the interactions between the polyelectrolyte chains. In addition, since the surfactant concentration is low, we can also neglect the interactions between the free surfactant molecules in the solution. Using these approximations, the Helmholtz free energy for the system under consideration can be written as a sum of different contributions

$$F = F^d + F^{\rm hc} + F^{\rm DH} + F^{\rm mix}, \tag{3}$$

where $F^d$ is the deformation free energy, $F^{\rm hc}$ is the excluded volume free energy, $F^{\rm DH}$ is the electrostatic contribution, and $F^{\rm mix}$ is the entropic free energy of the mixture.

The deformation free energy is obtained from the Flory–de Gennes theory [21,22],

$$\beta F^d = \sum_{i,j} N_{ij}\left(\frac{3}{2}(\alpha_{ij}^2-1) - 3\ln\alpha_{ij}\right), \tag{4}$$

where $\alpha_{ij}=R/R_0$ is the expansion factor of the polyelectrolyte chain belonging to the $ij$ complex, measured relative to the nonstrained Gaussian state, with radius $R_0=\sigma(Z-1)^{1/2}$. The extension of the chain, $R$, is given by

$$R = \sigma(Z-1)^{\gamma_{ij}}, \tag{5}$$

where the exponent $\gamma_{ij}$ is a measure of the deviation from the ideal limit for the $ij$ complex.

For the excluded volume interactions we consider only the particles forming the complexes. The $Z$ polyelectrolyte monomers, the $i$ condensed counterions, and the $j$ hydrophilic head groups of surfactant molecules interact through a virial expansion, while for the $jz_a$ hydrophobic neutral monomers we can use a free-volume interaction. Therefore, the corresponding excluded volume free energy, at low densities, can be approximated by

$$\beta F^{\rm hc} = \frac{2\pi\sigma^3}{3}\sum_{i,j}(Z+i+j)^2\frac{N_{ij}}{V_{ij}} - \sum_{i,j} jz_a N_{ij}\ln\left(1-\frac{2\pi\sigma^3}{3}\frac{jz_a}{V_{ij}}\right), \tag{6}$$

where $V_{ij}=4\pi R^3/3$ is the volume occupied by the $ij$ complex. We neglect the excluded volume interaction between the free particles (surfactant, counterions, and coions) in the solution.

Since the solution is very diluted, to obtain the electrostatic contribution, we take into account only the interactions between the free ions and the charges in the complexes. The corresponding free energy is calculated in the spirit of the Debye-Hückel-Bjerrum [17,18] and Manning theories [11,19],

$$\beta F^{\rm DH} = \lambda_B \sum_{i,j} N_{ij} p_{ij}^2 \mathcal{I}_{ij}, \tag{7}$$

where $\lambda_B=7.2$ Å is the Bjerrum length for water. In Eq. (7), $p_{ij}=-1+m_i+m_j$ is the net valence for each monomeric site along the polylectrolyte chain, with a fraction of $m_i=i/Z$ and $m_j=j/Z$ associated counterions and surfactants, respectively, and

$$\mathcal{I}_{ij} \equiv \int_0^Z (Z-x)\frac{e^{-\kappa r(x)}-1}{r(x)}dx, \tag{8}$$

where $r(x)=\sigma x^{\gamma_{ij}}$ and the inverse Debye screening length is given by $\kappa^2=4\pi\lambda_B(\rho_+ + \rho_- + \rho_{a,f})$. Since we are not allowing charge inversion in each monomeric site, $p_{ij}\leq 0$.

The entropic free energy is calculated from the partition function for a mixture of different species in the solution [25],

$$Q_{\rm mix} = \frac{(\zeta_+)^{N_+}(\zeta_-)^{N_-}(\zeta_{a,f})^{N_{a,f}}}{(N_+)!\,(N_-)!\,(N_{a,f})!}\prod_{i,j}\frac{(\zeta_{\rm cl})^{N_{ij}}}{(N_{ij})!}, \tag{9}$$

where $\zeta_s$ is the internal partition function of an isolated species $s$. For the free structureless counterions and coions, $\zeta_+ = \zeta_- = V/\Lambda^3$, where $\Lambda=h/\sqrt{2\pi m k_B T}$ is the mean thermal wavelength. For the unassociated surfactant molecules, for simplicity, we are taking $\zeta_{a,f}=V/\Lambda^3$.

To obtain the internal partition function of the complex, $\zeta_{\rm cl}$, we followed the procedure used in Refs. [10,11]. The electrostatic interaction between the charged entities in the complex is divided in two terms: an attractive part, responsible for the dipole formation and a repulsive one, due to the net charge on the polyelectrolyte monomeric sites. Since we have two different species, counterions and cationic surfactants, associating with the charged monomers, in principle, we can have two different types of dipoles in the complexes. For simplicity, we consider these dipoles as identical. In ad-

dition, we include an effective attraction between the surfactant molecules associated with different charged monomers on the polyelectrolyte chain. This attraction is originated by the hydrophobic interaction between the neutral monomers in the surfactant tails. Therefore, the internal partition function of the complex is written as

$$\zeta_{\mathrm{cl}} = \frac{Z!}{(Z-i-j)\,!\,i\,!\,j!}\frac{V}{\Lambda^3}\left(\frac{\zeta_2}{\Lambda^3}\right)^{i+j}\zeta_{\mathrm{r}}\zeta_{\mathrm{hy}}, \tag{10}$$

where $\zeta_2$ is the dipole associating constant [18],

$$\zeta_2 = \frac{2\pi\sigma^3}{3t^3}\left[\mathrm{Ei}\left(\frac{1}{t}\right) - \mathrm{Ei}(2) + e^2\right] - \frac{2\pi\sigma^3}{3}e^{1/t}\left(2+\frac{1}{t}+\frac{1}{t^2}\right), \tag{11}$$

with $t=\sigma/\lambda_B$. For the repulsive contribution, $\zeta_r$, we follow the approximations used in Refs. [10,11] in order to write

$$\ln\,\zeta_{\mathrm{r}} = -\frac{\lambda_B}{\sigma}p_{ij}^2\sum_{n=1}^{Z-1}\frac{Z-n}{n^{\gamma_{ij}}}, \tag{12}$$

where the sum is calculated using the Euler summation formula.

The hydrophobic contribution, $\zeta_{\mathrm{hy}}$, is calculated in the framework of the van der Waals theory [25]. Since the hydrophobic interaction is typically short ranged, we choose a square-well potential, $u_{\mathrm{hy}}$, to represent this attraction,

$$u_{\mathrm{hy}} = \begin{cases} \infty & r < \sigma_{\mathrm{eff}}, \\ -\varepsilon & \sigma_{\mathrm{eff}} \le r < 2\sigma_{\mathrm{eff}}, \\ 0 & r \ge 2\sigma_{\mathrm{eff}}, \end{cases} \tag{13}$$

where $\sigma_{\mathrm{eff}}=z_a^{1/3}\sigma$ represents the effective diameter of a sphere with the same volume as the surfactant tail and the strength, $\varepsilon$, represents the intensity of the hydrophobic interaction. Hence, the hydrophobic contribution to Eq. (10) is written as

$$\ln\,\zeta_{\mathrm{hy}} = \frac{14}{3}\pi\beta\varepsilon j^2\frac{z_a\sigma^3}{V_{ij}}. \tag{14}$$

We can add all these contributions, Eqs. (9)–(14), to write the mixing free energy as follows:

$$\beta F^{\mathrm{mix}} = \beta F^{\mathrm{id}} - \sum_{ij}(i+j)N_{ij}\ln\frac{\zeta_2}{\Lambda^3} + Z\sum_{i,j}N_{ij}(m_i\ln m_i + m_j\ln m_j - p_{ij}\ln|p_{ij}|) - \sum_{ij}N_{ij}\ln\zeta_{\mathrm{r}} - \sum_{ij}N_{ij}\ln\zeta_{\mathrm{hy}}, \tag{15}$$

where $\beta F^{\mathrm{id}}$ is the ideal gas free energy,

$$\beta F^{\mathrm{id}} = N_+\ln(\rho_+\Lambda^3) - N_+ + N_-\ln(\rho_-\Lambda^3) - N_- + N_{a,f}\ln(\rho_{a,f}\Lambda^3) - N_{a,f} + \sum_{ij}[N_{ij}\ln(\rho_{ij}\Lambda^3) - N_{ij}]. \tag{16}$$

### C. Thermodynamics of the system

The complex distribution is determined by the minimization of the Helmholtz free energy, Eq. (3), with respect to the number of particles of species $s$, $N_s$, and the extension of the complex, represented by the exponent $\gamma_{ij}$. The total number of possible combinations of $i$ and $j$, the number of associated counterions and surfactants, respectively, gives the number of possibilities for complex formation. It is straightforward to show that this number is $(Z+1)(Z+2)/2$, with the complex formation represented by the law of mass action,

$$\mu_{ij} = \mu_{00} + i\mu_+ + j\mu_{a,f}, \tag{17}$$

where $\mu_+$ and $\mu_{a,f}$ are the chemical potentials for unassociated counterions and surfactants in the solution, respectively, and $\mu_{00}$ is the chemical potential of a complex with no counterions and surfactants.

The minimization of Eq. (3) with respect to the exponent $\gamma_{ij}$ leads to

$$\frac{1}{N_{ij}}\frac{d\beta F}{d\gamma_{ij}} = 3(\alpha_{ij}^2-1)\ln(Z-1) - \frac{2\pi\sigma^3}{V_{ij}}(Z+i+j)^2\ln(Z-1) - \frac{2\pi\sigma^3}{V_{ij}}(jz_a)^2\left(1-\frac{2\pi\sigma^3}{3}\frac{jz_a}{V_{ij}}\right)^{-1}\ln(Z-1) + \lambda_B p_{ij}^2\mathcal{D}_{ij} + \frac{\lambda_B}{\sigma}p_{ij}^2\mathcal{S}_{ij} + \frac{14\pi\sigma^3}{V_{ij}}j^2z_a\beta\varepsilon\,\ln(Z-1) = 0, \tag{18}$$

where

$$\mathcal{D}_{ij} \equiv \int_0^Z (Z-x)\frac{\ln x}{r(x)}[1-e^{-\kappa r(x)}(\kappa r(x)+1)]dx, \tag{19}$$

and

$$\mathcal{S}_{ij} = \frac{Z^{2-\gamma_{ij}}}{(\gamma_{ij}-1)(2-\gamma_{ij})}\ln Z + \frac{Z^{2-\gamma_{ij}}-Z}{(1-\gamma_{ij})^2} + \frac{1}{720}[3\gamma_{ij}^2(1-Z) - 2Z(1+3\gamma_{ij}) - 1] - \frac{Z^{2-\gamma_{ij}}-1}{(2-\gamma_{ij})^2} + \frac{1}{12}(Z-1). \tag{20}$$

The law of mass action, Eq. (17), can be expressed in terms of the densities,

$$\rho_{ij} = \rho_{00}(\rho_+\sigma^3)^i(\rho_{a,f}\sigma^3)^j e^{-\beta\mu_{\mathrm{ex}}}, \tag{21}$$

where $\mu_{\mathrm{ex}}$ is the excess chemical potential derived from the Helmholtz free energy. The densities of the complexes, $\rho_{ij}$, and the extension exponents, $\gamma_{ij}$, can be determined from the numerical iteration of Eqs. (18) and (21) until convergence is obtained.

## III. RESULTS AND DISCUSSION

The density of monomers was fixed at $Z\rho_p=0.6$ $\mu$M, with $Z=64$, which corresponds to 2145 complexes. The monomer diameter was fixed at $\sigma=3$ Å. For the hydrophobic interaction, we have chosen $\varepsilon=3.6k_BT$, since for this hydrophobic strength we have found the transition at the same surfactant concentration as in Ref. [3]. The number of neutral

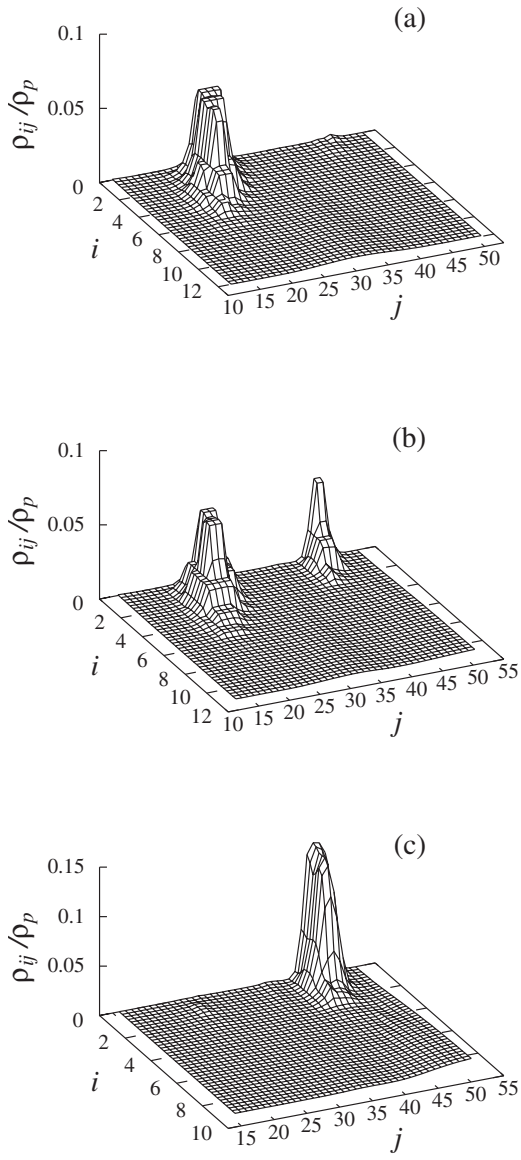


FIG. 1. Density distribution of the complexes, $\rho_{ij}/\rho_p$, as function of the number of associated counterions, $i$, and associated surfactant molecules, $j$, for a logarithm of surfactant concentration equal to (a) $\log_{10}\rho_a=-5.05$, (b) $\log_{10}\rho_a=-4.97$, and (c) $\log_{10}\rho_a=-4.85$. The hydrophobic strength is $\varepsilon=3.6k_BT$ and $Z=64$.

monomers in the hydrophobic tails of the surfactant molecules was fixed at $z_a=16$, corresponding to the CTAB surfactant [3]. The temperature of the system was maintained at 20 °C. These parameters are consistent with the experimental setup of Ref. [3], except for the number of polylectrolyte monomers. Since in our model the number of complexes scales as $Z^2/2$, we are restricted to small polyelectrolyte chains. Although the number of monomers $Z$ is small, using the same density of monomers, we expect to capture most of the experimental observations of Ref. [3].

In Fig. 1 we show the density distribution of the complexes, $\rho_{ij}/\rho_p$, for three typical surfactant concentrations. In Fig. 1(a) the surfactant concentration is low and the complexes contain small quantities of condensed counterions and surfactants. As a result, the distribution tends to be unimodal,

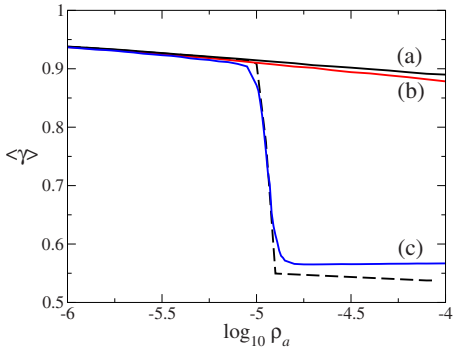


FIG. 2. (Color online) Average extension exponent of the complexes, $\langle\gamma\rangle$, as a function of the logarithm of surfactant concentration, for $Z=64$ and $\varepsilon=0$ (a), $2k_BT$ (b), and $3.6k_BT$ (c). We also include the case $Z=128$ for $\varepsilon=3.6k_BT$ (dashed line).

corresponding to the one-phase state. When we increase the surfactant concentration, we expect that association between the charged surfactant head groups and the polyelectrolyte charged monomers increases. In fact, for a certain surfactant concentration a bimodal density distribution appears, as shown in Fig. 1(b). There are two states sampled by the model, one at low and one at high numbers of condensed surfactant molecules, corresponding to a coexistence between these two states. As the surfactant concentration is further increased, the density distribution becomes unimodal once again, as shown in Fig. 1(c), and only complexes with high numbers of condensed surfactant are present.

In order to properly characterize these states, we calculate the extension of the complexes through the end-to-end distance, Eq. (5), and, equivalently, by the extension exponent $\gamma_{ij}$ associated with the $ij$ complex. In Fig. 2 we show the average value of these exponents, $\langle\gamma\rangle$. For a low surfactant concentration the complexes are extended, since the small number of associated ions, counterions, and free surfactant molecules, implies a small charge renormalization of the polyelectrolytes. As a result, the extension exponent is closer to the value associated with a rigid polyelectrolyte, $\langle\gamma\rangle=1$. For a high surfactant concentration the extension exponent decreases. Now the number of associated surfactant molecules is high, and the charge renormalization is strong. As a result, the complexes are found in a more compact configuration, with a value closer to the nonstrained Gaussian state, $\langle\gamma\rangle=0.5$. Between these two regimes, where the bimodal density distribution was found in Fig. 1(b), an abrupt conformational transition between these two states (extended and compacted) takes place at some critical surfactant concentration. With an increase of the polyelectrolyte size the transition becomes even more abrupt, as one can see in Fig. 2 for $Z=128$. It is interesting to see that the conformational transition is not only due to the electrostatic interactions, but also is strongly dependent on the hydrophobic effect described by Eqs. (13) and (14). In Fig. 2 we plot the average extension exponent with no hydrophobic interaction, $\varepsilon=0$, and for different values of the hydrophobic strength. Without hydrophobic interaction and for low hydrophobic strength, $\varepsilon \lesssim 3k_BT$, the abrupt conformational transition disappears completely, and the complexes become less extended continuously.

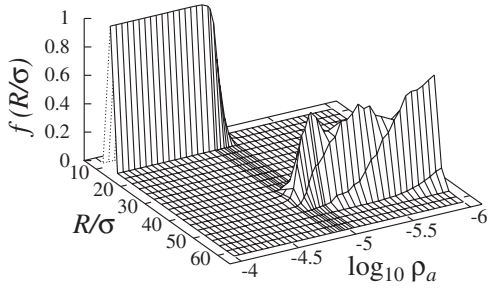


FIG. 3. Size distribution of the complexes, $f(R/\sigma)$, as a function of the logarithm of surfactant concentration. The hydrophobic strength is $\varepsilon=3.6k_BT$ and $Z=64$.

We can calculate the extension $R$ of the complexes, Eq. (5), as shown in Figs. 3 and 4. The regime of low surfactant concentration is identified with a highly swollen state, as shown in Fig. 4(a), due to the electrostatic repulsion between the charged monomers along the polyelectrolyte chains. According to Fig. 1(a), the number of associated counterions and surfactant is not high enough for an efficient complex compactation. If there is a sufficient amount of surfactant in the solution, polyelectrolyte charge renormalization becomes important, favoring a less extended configuration. For a high surfactant concentration, only compacted polyelectrolytes are observed, as shown in Fig. 3 and Fig. 4(c). Between these two limits, the extended and compacted states coexist in the solution, as shown in Fig. 3 and Fig. 4(b). The same bimodal size distribution and critical surfactant concentration were found experimentally in Ref. [3] and, most recently, in Refs. [7,8].

It is of interest to compare our results to the computer simulation studies of Ferber and Löwen [15,16] for the complex formation between ionic surfactant and a single polyelectrolyte chain. The same hydrophobic sensitivity of the complex size was observed in Ref. [16], where a similar short-range hydrophobic attraction between the tail beads was introduced. Depending on the strengths of both electrostatic and the hydrophobic interactions, a transition occurs between a cylindrical shape and a spherical micellar complex. Although the transition reported in Ref. [16] is very similar to the transition observed in this paper, there are important differences between our model and this prior study. First, the hydrophobic attraction in Ref. [16] is introduced bead by bead, while in our model we have used a mean-field approach. Therefore, we do not expect to have the same hydrophobic strength at the transition. The value used in this paper reproduces approximately the critical surfactant concentration found in Ref. [3]. Second, our model is unable to characterize properly the shapes of the complexes, since we do not include the micelle formation. We do not have free micelles in the solution and the low extension exponent of the complexes in Fig. 2 is associated with a compacted structure. In Ref. [16] there are free micelles and at high hydrophobicity the compacted structure is identified with a spherical micelle, composed by a neutral core of surfactant tails and a charged corona of surfactant heads, with the polyelectrolyte chain wrapped around.

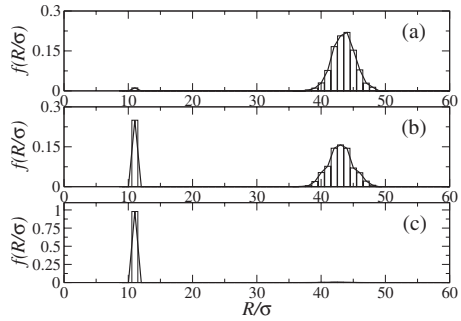


FIG. 4. Size distribution of the complexes, $f(R/\sigma)$, for the same parameters used in Fig. 1.

## IV. CONCLUSIONS

In summary, the complexation between flexible polyelectrolytes and cationic surfactants has been studied in the framework of the Debye-Hückel-Bjerrum-Manning and Flory theories. Allowing for the association between the charged polyelectrolyte monomers and the free counterions and surfactants in the solution, complex formation is observed, in which one cluster is created by a polyelectrolyte chain and a distribution of condensed counterions and surfactant molecules. The different types of complexes, with respective size and density distributions, have been obtained as a function of the surfactant concentration. As a result of the complexation the charge of the polyelectrolyte is renormalized and its extension decreases when the surfactant concentration increases. In particular, when we included a hydrophobic interaction between the neutral monomers on different condensed surfactant tails we have found a discrete conformational transition from an extended state to a collapsed state at some critical surfactant concentration.

While the broad outline of the phase behavior is consistent with experimental observations [3], a quantitative comparison between our results and these predictions must be done with caution, since the simple model used in this work does not consider some important factors. The persistence length of the DNA, since these molecules have an intrinsic rigidity, their double helix structure, realistic sizes for the DNA molecules and the presence of salt in the solution still remain important effects and need to be explored in the future.

## ACKNOWLEDGMENTS

One of the authors (A.D.) acknowledges financial support of the Brazilian agency CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico). Funding by FAPERGS (Fundação de Amparo à Pesquisa do Rio Grande do Sul) [through Contract No. 0412236 (PROAPP FAPERGS/CNPq) to P.S.K.] is also gratefully acknowledged.

[1] D. Lasic, *Liposomes in Gene Delivery* (CRC, Boca Raton, FL, 1997).
[2] C. Bustamante, J. F. Marko, E. D. Siggia, and S. Smith, Science **265**, 1599 (1994).
[3] S. M. Mel'nikov, V. G. Sergeyev, and K. Yoshikawa, J. Am. Chem. Soc. **117**, 2401 (1995).
[4] A. V. Gorelov, E. D. Kudryashov, J.-C. Jacquier, D. McLoughlin, and K. E. Dawson, Physica A **249**, 216 (1998).
[5] Y. S. Mel'nikova and B. Lindman, Langmuir **16**, 5871 (2000).
[6] Z. X. Wang, D. J. Liu, and S. J. Doug, Biophys. Chem. **87**, 179 (2000).
[7] S. Marchetti, G. Onori, and C. Cametti, J. Phys. Chem. B **109**, 3676 (2005).
[8] S. Marchetti, G. Onori, and C. Cametti, J. Phys. Chem. B **110**, 24761 (2006).
[9] P. S. Kuhn, Y. Levin, and M. C. Barbosa, Chem. Phys. Lett. **298**, 51 (1998).
[10] P. S. Kuhn, Y. Levin, and M. C. Barbosa, Macromolecules **31**, 8347 (1998).
[11] P. S. Kuhn and M. C. Barbosa, Physica A **357**, 142 (2005).
[12] H. Diamant and D. Andelman, Europhys. Lett. **48**, 170 (1999).
[13] P. Hansson, Langmuir **17**, 4167 (2001).
[14] M. B. Silva, L. S. Lucena, and M. C. Barbosa, Physica A **331**, 42 (2004).
[15] C. von Ferber and H. Löwen, J. Chem. Phys. **118**, 10774 (2003).
[16] C. von Ferber and H. Löwen, Faraday Discuss. **128**, 389 (2005).
[17] P. W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
[18] N. Bjerrum, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **7**, 1 (1926).
[19] G. S. Manning, J. Chem. Phys. **51**, 924 (1969).
[20] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).
[21] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1971).
[22] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
[23] C. E. Lin, J. Chromatogr., A **1037**, 467 (2004).
[24] A. Cifuentes, J. L. Bernal, and J. C. Diez-Masa, Anal. Chem. **69**, 4271 (1997).
[25] T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986).