Cylindrical DNA with cationic surfactant and micelle formation

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Abstract

The association of cationic surfactant to cylindrical DNA is studied, in the basis of Debye-Huckel, Bjerrum and Manning theories. Electrostatic interaction is the leading interaction in the association of cationic surfactant, and hydrophobicity determines the cooperativity of the process with an energy parameter ε between surfactants in the complex. Hydrophobic interaction between surfactants in solution leads to micelle formation, with a second energy parameter ε_m. The hydrophobic interaction parameters in complex formation and micelle formation are estimated through the binding isotherms, which are compared with experimental curves.

Keywords: DNA, polyelectrolytes, charged systems, surfactants
64.70.qd Thermodynamics and statistical mechanics
64.70.km Polymers
64.70.pv Colloids

1 Introduction

Polyelectrolyte solutions are very important systems in physics, chemistry and biology, as well in industry [1]-[13]. These systems consist of macromolecules that in solution become highly ionized. A central difficulty in

studying these systems is the long-ranged coulomb interaction, and the presence of several other chemical species also contributes to increase this difficulty. Nevertheless these systems have been intensively studied in the literature [14]-[27]. If the molecules are flexible, the large number of configurations makes the problem much more difficult to address [28]-[31].

A fundamental polyelectrolyte system in biology is an aqueous solution of DNA molecules. Among several applications we can cite the development of gene delivery systems [32]. A common feature in DNA solutions is the presence of many chemical species, as salt and surfactants, which determine the configuration of DNA molecules. The transition of DNA from a collapsed state to an extended state is an important fact in these systems, since the collapse of DNA is a prerequisite to allow, in principle, the successfull gene transfer across cellular membrane. Cationic surfactant molecules, for example cetyltrimethylammonium bromide (CTAB), may be used in this process, since the hydrophobic attraction between surfactants leads to micelle formation, and electrostatic attraction to negatively charged DNA forms complexes that are several times smaller than the extended molecule. In the decompaction of DNA it can be used, for example, monovalent salt, anionic surfactant, or cyclodextrins. In all these systems not only the electrostatic interaction occurs, but there is also hydrophobic interaction. This leads to cooperative association of surfactants in DNA, for example, and to decompaction of DNA previously compacted with cationic surfactant, when anionic surfactant, salt, or cyclodextrin is added to the system. Solutions of DNA with surfactant and salt have been intensively studied, in experiments, theory and numerical analysis [33]-[52].

We have proposed previously a model for flexible polyelectrolytes in solution with salt and cationic surfactant [30, 31]. The complex distribution for the system neglecting micelle formation was evaluated, and a one cluster size approximation was used when micelle formation was considered. For cylindrical molecules the situation is a little better, since the spatial configurations of the molecules does not matter. Recently a model has been proposed for solutions of rigid polyelectrolytes [53]-[56]. The model is based on Debye-Huckel, Bjerrum, and Manning ideas [57]-[62]. In this way it is possible to evaluate the distribution function ρ_i of complexes in DNA solutions with ions [55], and also to evaluate the binding isotherms of DNA with cationic surfactants and ions, which has been done using a one size approximation [56].

In this work we evaluate the distribution function ρ_{ij} of complexes of rigid DNA molecules with surfactants and positive ions, and construct the binding isotherms. We consider cationic surfactants. The electrostatic interaction is an important factor in the complex formation, mainly for cationic surfac-

tants, while hydrophobic attraction between associated surfactants leads to a cooperative association [56]. The DNA molecules are considered here as cylindrical, hence we have the advantage of no concern with spatial configurations of DNA molecules.

The structure of this work is as follows. In section 2 we write the free energy for micelle formation. In section 3 we write the free energy of polyelectrolyte solution, obtaining the complex distribution Here we state the free energy and show how the complex distribution is evaluated. Section 4 discuss the results and present the conclusions.

2 The free energy of micelles

We follow the same approach in [31], where we evaluated the free energy of micelle before to consider polyelectrolyte solution. This is a simplification of the problem, but since the density of polyelectrolytes is not too large, it is a good approximation, since it avoids the more complicated task of minimize a full free energy with all parameters together. Here we construct the free energy for micelles, without polyelectrolytes. Once we find the fraction of micelles and its charge, we consider the polyelectrolyte solution with these parameters fixed. The densities satisfy the relations,

$$\begin{aligned}
\rho_+ &= \rho_s \,, \\
\rho_- &= \rho_s + \rho_a - Z_g m_g \rho_g \,, \\
\rho_{af} &= \rho_a - Z_g \rho_g \,, \\
\rho_g &= \frac{f \rho_a}{Z_g} \,,
\end{aligned} \tag{1}$$

The free energy of micelles is written as a sum of terms,

$$F_m = F_{id}^m + F_{dh}^m + F_{el}^m + F_{int}^m \,. \tag{2}$$

The ideal free energy is,

$$\begin{aligned}
\beta F_{id}^m &= \sum_s N_s (\ln \rho_s^* - 1) \,, \\
&= N_+ (\ln \rho_+^* - 1) + N_- (\rho_-^* - 1) \\
&\quad + N_{af} (\ln \rho_{af}^* - 1) + N_g (\ln \rho_g^* - 1) \,.
\end{aligned} \tag{3}$$

The free energy describing the interaction between charged particles in the solution is given by the Debye-Hückel term,

$$\beta F_{dh}^{m} = -\frac{1}{4\pi}\left[\ln(1+\kappa\sigma) - \kappa\sigma + \frac{(\kappa\sigma)^2}{2}\right], \tag{4}$$

where the inverse Debye screening lenght κ^{-1} is defined as usual,

$$\kappa^2 = 4\pi\lambda_B(\rho_+ + \rho_- + \rho_{af}). \tag{5}$$

The electrostatic contribution describing the interaction between micelles and the solution is,

$$\beta F_{el}^{m} = -\frac{1}{2}Z_g^2 N_g \frac{\lambda_B}{\sigma}(1-m_g)^2 \frac{\kappa\sigma}{1+\kappa R_g}, \tag{6}$$

and,

$$R_g = \left(\frac{3}{4\pi}Z_g v_a\right)^{1/3}, \tag{7}$$

$$v_a = \frac{\pi}{6}(1+z_a)\sigma^3. \tag{8}$$

The internal free energy F_{int}^{m} of micelles is,

$$F_{int}^{m} = F_{ion}^{m} + F_{ent}^{m} + F_{h}^{m} + F_{cs}^{m} + F_{a}^{m}. \tag{9}$$

The electrostatic term is,

$$\beta F_{ion}^{m} = Z_g^2 N_g \frac{\lambda_B}{\sigma}\frac{1}{2R_g}(1-m_g)^2. \tag{10}$$

The entropic free energy is,

$$\beta F_{ent}^{m} = Z_g N_g m_g \ln(m_g) + Z_g N_g (1-m_g)\ln(1-m_g), \tag{11}$$

The hydrophobic free energy is,

$$\beta F_{h}^{m} = -\frac{14}{3}\pi\beta\varepsilon_m Z_g^2 N_g \frac{z_a}{V_g}, \tag{12}$$

with,

$$V_g = \frac{4\pi}{3}R_g^3. \tag{13}$$

The excluded volume free energy is given by the Carnahan-Starling expression,

$$\beta F_{cs}^{m} = (N_+ + N_- + N_{af} + N_g)\frac{y(4-3y)}{(1-y)^2}\,, \tag{14}$$

with,

$$y = \frac{\pi}{6}\bar{\sigma}^3(\rho_+ + \rho_- + \rho_{af} + \rho_g)\,, \tag{15}$$

and,

$$\bar{\sigma} = \frac{\rho_+ + \rho_- + \rho_{af}\sigma_a + \rho_g 2R_g}{\rho_+ + \rho_- + \rho_{af} + \rho_g}\,, \tag{16}$$

$$\sigma_a = (1+z_a)^{1/3}\sigma\,. \tag{17}$$

Finally, the association free energy is given by the Bjerrum theory,

$$\beta F_a^m = -Z_g N_g m_g \ln(\zeta/\sigma^3)\,, \tag{18}$$

with the association constant,

$$\begin{aligned}\zeta &= \frac{4\pi}{3}\left\{\frac{\exp(2)}{2T^{*3}} - \exp(1/T^*)\left[1 + \frac{1}{2T^*} + \frac{1}{2T^{*2}}\right]\right. \\ &\left. + \frac{1}{2T^{*3}}[Ei(1/T^*) - Ei(2)]\right\}\,,\end{aligned} \tag{19}$$

for $\lambda_B/\sigma > 2$ and $T^* = \sigma/\lambda_B$.

3 The free energy of polyelectrolyte solution

The model system is essentially the same previously studied by us [55, 56]. We have a solution of cylindrical DNA molecules, positive counterions, surfactants and possibly monovalent salt. DNA molecules are represented by rigid cylinders of length $L = Zb$ and radius a. We take as typical values $b = 1.7$ Å and $a = 10$ Å. The number of sites in each DNA molecule is Z, hence there are Z positive counterions for each DNA molecule, since the whole system is neutral. All monomers, both of ions or in surfactant molecules, are taken as spheres of diameter $\sigma = 3$ Å. The solvent is a continuous medium with permittivity $\varepsilon_s = 78.5\,\varepsilon_0$, representing water, and the temperature is 25^{o}C.

At thermodynamic equilibrium there are complexes of DNA with associated surfactants and ions, and free molecules in solution. The association of ions is determined by electrostatic interaction between charged sites of DNA

and ions, and this process is not cooperative. The association of cationic surfactant is determined by electrostatic attraction, while the cooperativity in the process is determined by hydrophobic attraction between associated surfactants. The association of anionic and neutral surfactants to DNA is due to hydrophobic interaction, since there is electrostatic repulsion between anionic surfactants and DNA, and no electrostatic interaction of DNA with neutral surfactants. In all cases, the cooperative association is determined by hydrophobic attraction between associated surfactants in DNA complexes. The number density of a complex ij is denoted by $\rho_{ij} = N_{ij}/V$, where N_{ij} is the number of complexes with i associated positive ions and j associated surfactants, and V is the volume. The corresponding association fractions are $m_i = i/Z$ and $m_j = j/Z$. These are in fact mean association fractions, since the associated particles are considered uniformly distributed along the DNA molecule, i.e., we are not concernet with each particle is in each site, only the total numbers i and j for a complex are important. However, if desired this can also be evaluated [55]. We have also the normalization condition

$$\sum_{ij} \rho_{ij} = \rho_p \,, \tag{20}$$

where $\rho_p = N_p/V$ is the number density of DNA molecules. The corresponding density of DNA monomers is then $\rho_m = Z\rho_p$. The range of summation in the above equation depends on the particular case in study. The system contains cationic surfactants and ions associating in DNA molecules, with no more than one particle per site.

This system has yet been studied by us previously, but only in the one size approximation [56]. The size distribution ρ_i was evaluated only for solutions of DNA with ions [55]. Here we obtain explicitly the distribution ρ_{ij} for complexes of DNA with surfactants and ions. Note that we have positive and negative ions in the system. Figure 1 shows schematically the system. We have at most one particle per site.

The several number densities in the system satisfy the equations

$$\begin{aligned}
\rho_+ &= Z\rho_p + \rho_s - \sum i\rho_{ij} \,, \\
\rho_- &= \rho_a + \rho_s - Z_g m_g \rho_g \,, \\
\rho_{af} &= \rho_a - \sum j\rho_{ij} - Z_g \rho_g \,, \\
\rho_g &= \frac{f\rho_a}{Z_g} \,,
\end{aligned} \tag{21}$$

where ρ_{af} is the number density of free surfactants, ρ_+ of positive ions, and ρ_- of negative ions. The number density of surfactants is ρ_a, and of ionic

pairs of salt is ρ_s. Since we allow no more than one associated molecule per DNA site, we have $i + j \leq Z$. With this restriction the total number of possible complexes is

$$N_c = \frac{1}{2}(Z+1)(Z+2)\,. \tag{22}$$

If $Z = 50$, for example, we have 1326 possible complexes, and for $Z = 100$ this number increases to 5151, and each summation in the above equations will have the corresponding number of terms. Below we consider $Z = 100$ for DNA with cationic surfactant, $Z = 80$ for DNA with anionic surfactant, and $Z = 70$ for neutral surfactant. This is done in order to facilitate the complex distribution evaluation, since increasing Z increases obviously the number of possible complexes. Although real DNA molecules can be much larger than this, we will consider real monomer densities, hence we expect this is not a shortcoming. After all, the results will prove to be at least qualitatively correct.

The inverse Debye screening length is

$$\kappa^2 = 4\pi\lambda_B(\rho_+ + \rho_- + \rho_{af})\,, \tag{23}$$

where $\lambda_B = \beta q^2/4\pi\varepsilon_s$ is the Bjerrum length. Other parameters are q, the proton charge, and $\beta = 1/kT$, with k the Boltzmann constant.

We write the Helmholtz free energy of the system as a sum of contributions,

$$F = F_{id} + F_{ent} + F_{ion} + F_h + F_{el}\,. \tag{24}$$

The ideal term is simply

$$\beta F_{id} = \sum N_k[\ln\rho_k^* - 1]\,, \tag{25}$$

with the summation extending over all present species, and we define the dimensionless density of species k as $\rho_k^* = \rho_k\sigma^3$. Hence,

$$\begin{aligned}\beta F_{id} \;=\; & \sum_{ij} N_{ij}[\ln\rho_{ij}^* - 1] \\ & + N_+(\ln\rho_+^* - 1) + N_-(\ln\rho_-^* - 1) \\ & + N_{af}(\ln\rho_{af}^* - 1)\,.\end{aligned} \tag{26}$$

The entropic term F_{ent} describes all possible configurations for i ions and j surfactants at Z sites, with the restriction of at most one particle per site.

This will be changed below for anionic and neutral surfactants. The number of configurations is then

$$\Omega_{ij} = \frac{Z!}{i!j!(Z-i-j)!}\,, \tag{27}$$

which leads to

$$\begin{aligned}
\beta F_{ent} &= -\sum_{ij} N_{ij} \ln \Omega_{ij}\,, \\
&= Z \sum_{ij} N_{ij}[m_i \ln m_i + m_j \ln m_j \\
&\quad +(1-m_i-m_j)\ln(1-m_i-m_j)]\,.
\end{aligned} \tag{28}$$

The electrostatic interaction between sites of the DNA molecule is described by

$$\beta F_{ion} = \frac{\lambda_B}{b} \mathcal{S} \sum_{ij} N_{ij} p_{ij}^2\,, \tag{29}$$

where the valence of each site of a ij complex is

$$p_{ij} = -1 + m_i + m_j\,, \tag{30}$$

and

$$\mathcal{S} = \frac{1}{2} \sum_{i \neq j}^{Z} \frac{1}{|i-j|} = Z[\psi(Z) - \psi(1)] - Z + 1\,, \tag{31}$$

with ψ the digamma function [63]. Note that the above sum is done over one chain, and has the same value for all chains. This is a direct consequence of taking associated particles uniformly distributed along the DNA chain. That is, a ij complex has all sites with the same valence p_{ij}.

The hydrophobic interaction between associated surfactants is a cooperative phenomena, and we approximate this contribution by [56]

$$\beta F_h = -\beta\varepsilon(Z-1) \sum_{ij} N_{ij} m_j^2\,. \tag{32}$$

The energy ε is an adjustable parameter, which fixes the transition in surfactant association to DNA. A term like this leads to a discontinuous transition in the binding isotherm, in the one size approximation [56]. When evaluated exactly, this contribution leads to a smooth transition [64]. We shall see that

the above free energy contribution leads to a smooth transition after the complex distribution is found, with no need to evaluate exactly its contribution to the free energy of the system.

The electrostatic interaction between complexes and the ionic solution is given by a Debye-Huckel term [55, 56, 65, 66],

$$\beta F_{el} = \frac{Z\lambda_B}{b} \frac{K_0(\kappa a)}{\kappa a K_1(\kappa a)} \sum_{ij} N_{ij} p_{ij}^2 \,, \tag{33}$$

with K_n the modified Bessel function of second kind [63].

The complete free energy of the system is then a function of the densities,

$$F = F(\{\rho_{ij}\}, \rho_{af}, \rho_+, \rho_-) \,. \tag{34}$$

The configuration equilibriu is obtained minimizing the free energy with respect to the densities, which leads to the mass action law,

$$\rho_{ij}^* = (\rho_+^*)^i (\rho_{af}^*)^j \exp\{-\beta(\mu_{ij}^{ex} - i\mu_+^{ex} - j\mu_{af}^{ex})\} \,, \tag{35}$$

where the $\mu' s$ are the chemical potentials. We solve the above equations iteratively, obtaining then the complex distribution ρ_{ij}.

Once the complex distribution has been obtained we may evaluate the mean values of i and j, or the mean association fractions,

$$\bar{m_i} = \frac{1}{Z\rho_p} \sum_{ij} i\rho_{ij} \,, \qquad \bar{m_j} = \frac{1}{Z\rho_p} \sum_{ij} j\rho_{ij} \,. \tag{36}$$

We can also define the complex distribution

$$f_{ij} = \frac{\rho_{ij}}{\rho_p} \,, \tag{37}$$

and write $\bar{m_i} = \sum_{ij} m_i f_{ij}$, etc.

4 Results and Conclusions

The results obtained for DNA with cationic surfactant are shown in figures 1-5. We use the experimental densities of [33] and [34]. We denote the system in [33] as System I, in which we have $\rho_m = 2$ mM, $\rho_s = 20$ mM, $z_a = 12$, $\rho_{a,c} = 2.5$ mM, $\rho_{af,c} = 1.5$ mM. We obtain this transition in our model for $\beta\varepsilon = 3.3$. The system in [34] is denoted as System II, in which we have $\rho_m = 0.616$ mM, $\rho_s = 20$ mM, $z_a = 12$, $\rho_{a,c} = 1.208$ mM, $\rho_{af,c} = 0.9$ mM. We obtain this transition for $\beta\varepsilon = 3.86$. In both cases we use $\beta\varepsilon_m = 0.53$.

We fix $Z = Z_g = 100$ and $T = 25^o$C. These two transitions are shown in figure 1. Note that we have $\bar{m}_i + \bar{m}_j \leq 1$. The shape of the figures is typical of a cooperative association, determined by the energy parameter ε between associated surfactants in the complex. The fraction f of micelles in solution and the association fraction m_g of negative ions on the micelles are also shown. Figures 2 and 3 shown the complex distribution as functions of i and j, respectively, at the maximum value of the distribution fraction f_{ij} of complex ij. Figures 4 and 5 shows the critical density of surfactants $\rho_{a,c}$(M) as function of $\beta\varepsilon$ for systems I and II, respectively. For system I we show two fittings, linear and quadratic, while for system II the linear fitting is sufficient. For system I we obtain,

$$\rho_{a,c}(M) = 6.8433 - 1.3286\beta\varepsilon\,, \tag{38}$$

and,

$$\rho_{a,c}(M) = -9.94 + 9.3589\beta\varepsilon - 1.6964(\beta\varepsilon)^2\,. \tag{39}$$

For system II we have,

$$\rho_{a,c}(M) = 4.0835 - 0.74869\beta\varepsilon\,. \tag{40}$$

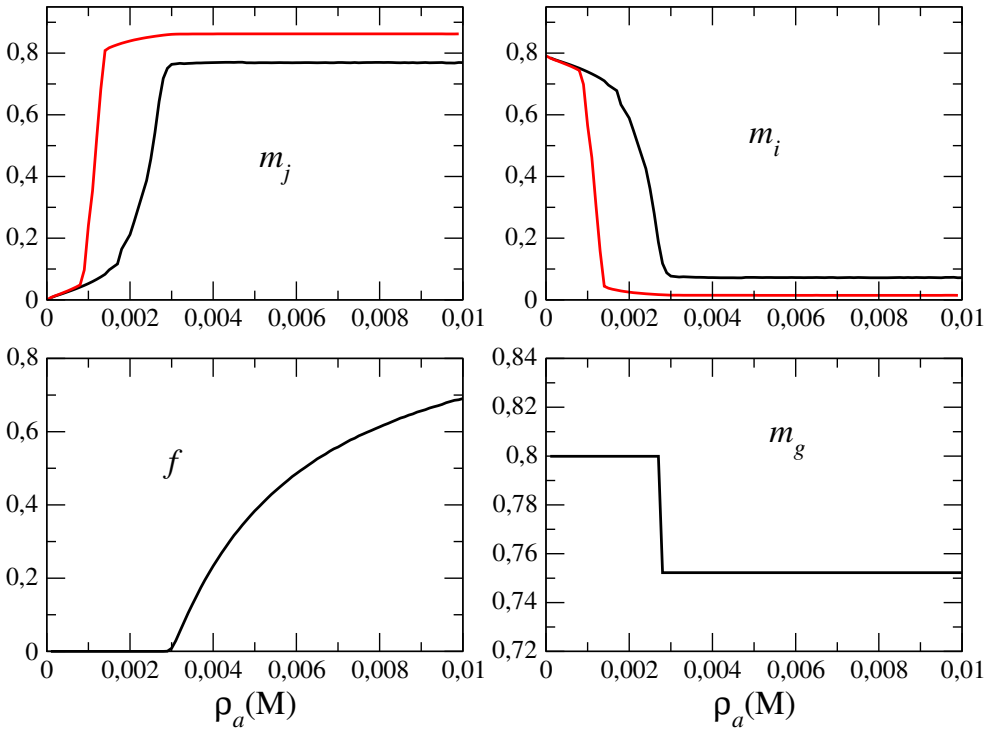

Fig. 1. Mean association fractions of surfactant m_j and ions m_i for systems I (black line) and II (red line), fraction f of surfactants in micelles and mean association fraction m_g of negative ions at micelles, as functions of ρ_a.

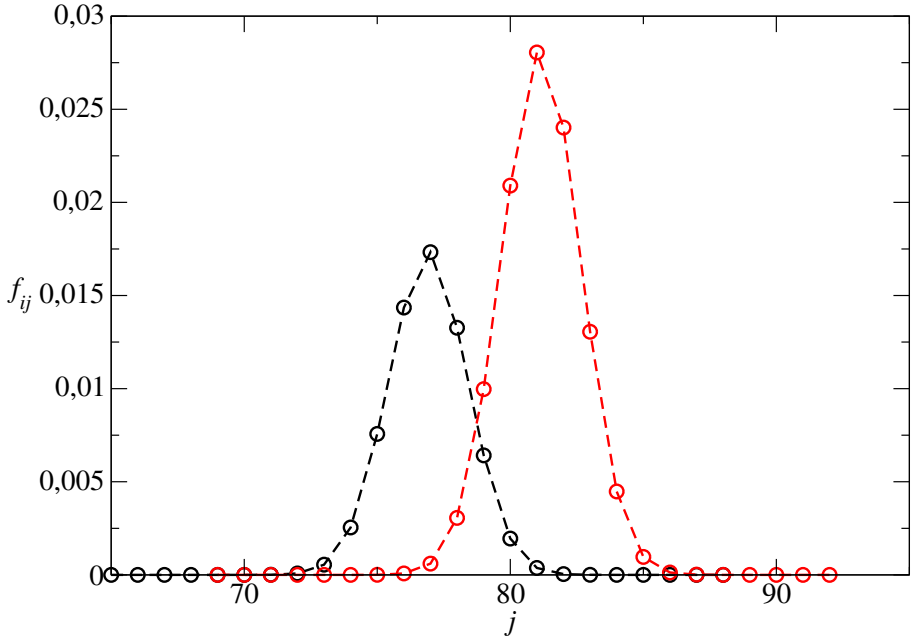

Fig. 2. Fraction f_{ij} of complex ij as function of j at the maximum value of f_{ij}, for systems I, $i = 7, j = 77$ (black line) and II, $i = 4, j = 81$ (red line).

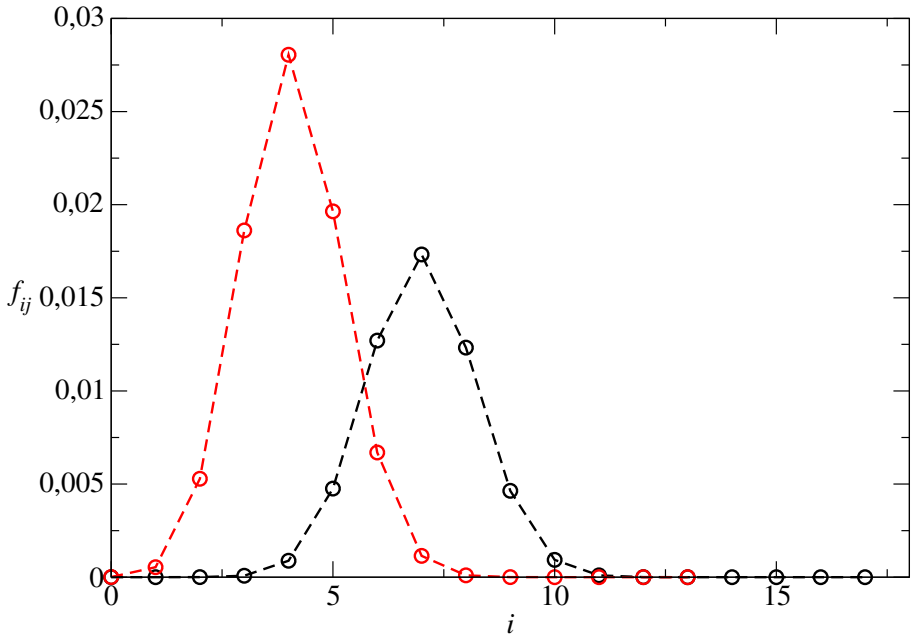

Fig. 3. Fraction f_{ij} of complex ij as function of i at the maximum value of f_{ij}, for systems I, $i = 7, j = 77$ (black line) and II, $i = 4, j = 81$ (red line).

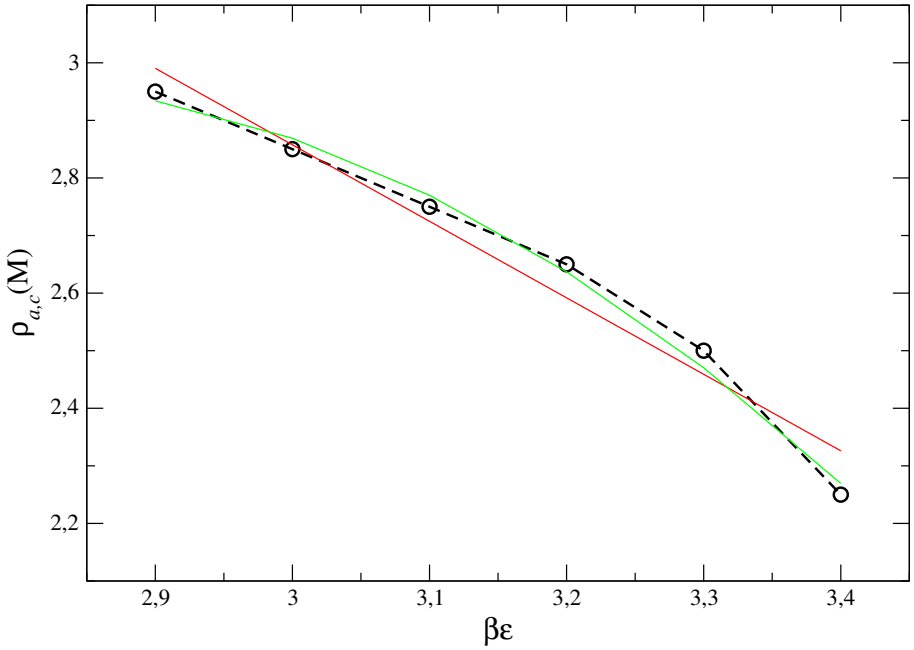

Fig. 4. Critical density of surfactant as function of $\beta\varepsilon$ for system I.

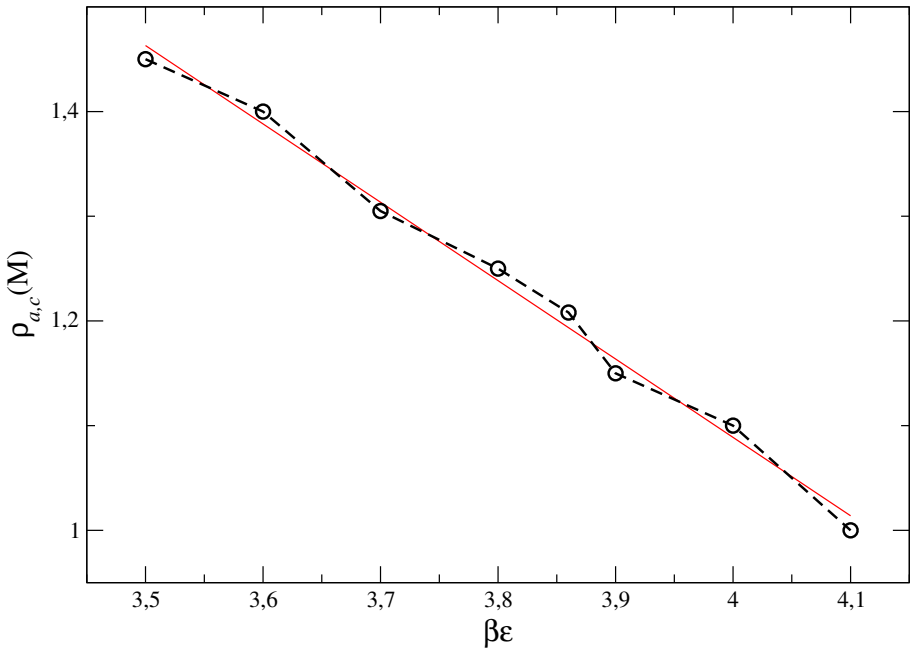

Fig. 5. Critical density of surfactant as function of $\beta\varepsilon$ for system II.

In conclusion, we have estimated the values of hydrophobic interactions in DNA surfactant systems. For cationic surfactants, the main interaction responsible for complex formation is the electrostatic attraction between DNA and surfactants. The cooperative association of surfactants is determined by the hydrophobic energy parameter ε, between associated surfactants in the complex. In the solution, micelle formation is determined by a second hydrophobic parameter ε_2.

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