

Charged Micelles in Salt-Free Dilute Solutions

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ABSTRACT: We study micelles in salt-free dilute aqueous solutions of diblock copolymers made of long charged A chains and short hydrophobic B chains. The number density of aggregates with p chains (n_p) and the number of condensed counterions in a p -aggregated chain ($N_c(p)$) are obtained equating the chemical potentials of the p -aggregated chains ($p = 2, 3, \dots$) with those of the free chains ($p = 1$) and equating the chemical potentials of the condensed counterions in the aggregates ($p = 1, 2, \dots$) with those of the free counterions. The critical micelle concentration (cmc) and the degree of polydispersity are large in charged diblock copolymer solutions. Since $N_c(p)$ increases as p increases, micelles with $p \gg 1$ are nearly neutral. The most populated micelles in experimentally accessible systems, however, have a small number of chains and their effective charge is not strongly reduced. As the concentration of copolymer increases above the cmc, the concentration of free chains decreases.

I. Introduction

Diblock copolymers in selective nonpolar solvents form micelles.^{1–4} Micellization occurs when the diblocks are made of a B block in a poor solvent chemically linked to a solvated A block. If the degrees of polymerization of the A and B blocks, N_A and N_B , respectively, are such that $N_A \gg N_B$, a homogeneous suspension of rather monodispersed micelles with a small core radius R_B and a swollen corona radius R_A results when the concentration of copolymer is higher than the critical micelle concentration (cmc). The micelles have “starlike” conformations.¹ That is, p chains aggregated in a micelle have the conformation of p chains chemically linked (star macromolecule) in solution:⁵

$$R_A(p) \propto ap^{1/4}(fN)^{1/2}, \quad \text{for an A-}\Theta \text{ solvent} \quad (1a)$$

$$R_A(p) \propto ap^{1/5}(fN)^{3/5}, \quad \text{for an A-good solvent} \quad (1b)$$

where a is the characteristic size of the A monomers, assumed here to be equal to the characteristic size of the B monomers, and $f = N_A/N$, where $N = N_A + N_B$.

A–B diblock copolymers in A-good solvents are ideal candidates to stabilize colloidal suspensions. Spontaneous coagulation is prevented by attaching the short B block to the colloidal particle. In order to stabilize colloidal suspensions in polar solvents (such as latex paint in aqueous solutions), water soluble A blocks must be used. Highly charged chains at zero or low salt concentrations are water soluble if the counterions and/or salt ions are monovalent.^{6,7} The properties of charged–neutral diblock copolymers in polar solvents at zero or low salt concentrations are not understood. As explained below, it has been argued that if $f > (1 - f)$ and/or $N \gg 1$, micelles cannot form.⁸ Recent experimental studies, however, suggest the existence of micelles in this limit.^{9,10} In this paper we study micellization in charged–neutral diblock salt-free aqueous solutions and compare our results to micellization in noncharged A–B copolymers in nonpolar solvents.

In the limit of high salt concentrations, Dan and Tirrel¹¹ found that the charged–neutral diblock copolymer micelles in polar solvents have similar properties to those of noncharged diblock copolymers in nonpolar solvents.¹² In salt-free and/or low salt concentration solutions, however, the electrostatic interactions are not screened. In this limit, the ions are not homogeneously mixed but some are strongly attracted to the charged chains (ion condensation), reducing the effective charge of the chains.¹³ The driving force for aggregation in charged copolymers, a reduction in the interfacial energy between the B monomers and the solvent, overcomes the electrostatic energy increase in this limit only if it is strongly reduced by ion condensation. We find here that for copolymers with $fN \gg 1$, only if the number of condensed ions per chain in a p -aggregated chain ($N_c(p)$) increases rapidly as p increases, can the chains aggregate in micelles. The fluorescence spectra of diblock copolymer micellar aqueous solutions suggest that indeed the number of condensed counterions per chain in the micelles is much larger than that in the free chains.⁹

Marko and Rabin constructed a model of monodisperse micelles with $p \gg 1$ A–B diblock copolymer chains with fully charged A blocks in salt-free (or low salt concentration) dilute solutions.⁸ They assumed that the micelles are nearly neutral ($N_c(p) \approx N_A = fN$) and that there is no ion condensation in the free chains ($N_c(p=1) = 0$). Also, in their model the condensed counterions were assumed to move freely in the corona of the micelles, generating a counterion pressure which fully stretches the corona ($R_A = afN$). Micelles with fully stretched A chains are unphysical when $f \gg (1 - f)$. Neutral aggregates with $f \gg (1 - f)$, for example, have stretched A chains only if $p > (fN)^2$,⁴ which is an unphysically large value for the most probable micelle aggregation number, p^* (neutral A blocks in nonpolar solvents have $p^* \propto N^\alpha$ with $0 < \alpha < 1$). The model of Marko and Rabin gives $p^* \propto (1 - f)^2/(f^2N)$ at the cmc, contradicting the assumption that $p^* \gg 1$. Therefore, only extremely short chains with $f \ll (1 - f)$ form micelles in their model. Charged micelles, however, are not monodisperse, nor are the condensed counterions free to explore the corona volume, as explain below.

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Stevens and Kremer recently showed by molecular dynamics simulations of linear polyelectrolyte solutions that the counterions follow the path of the charged chains.¹⁴ Furthermore, the simulations showed clearly that the Debye–Huckel approximation is not valid because it does not describe ion condensation. We use here a renormalized Debye–Huckel approach recently developed to describe solutions of charged chains.^{15a} The model is known to describe properly salt-free colloidal suspensions^{15b} and is in agreement with the results obtained by Stevens and Kremer. We construct the free energy of a polydisperse micelle system and obtain the number density of aggregates with p chains, n_p , equating the chemical potential of the chains in the micelles ($p = 2, 3, \dots$) with that of the free chains ($p = 1$). The number of condensed counterions per chain, $N_c(p)$, is obtained equating the chemical potential of the condensed counterions with that of the free counterions. With this model we find that the degree of polydispersity is large in charged A block micelles because the number of degrees of freedom of the system increases by allowing the number of condensed counterions to depend on p . Since aggregation is observed when the chain concentration is sufficiently high for ion condensation to occur (in the limit of infinite dilution there is no ion condensation in finite size chain systems), the cmc is large in comparison with that for noncharged A block micelles in nonpolar solvents. We find that if $p \gg 1$, the micelles have nearly zero effective charge and they have the “starlike” conformation given in eq 1. If p is small, however, the micelles are stretched. For most experimentally accessible systems the most populated micelles have few chains.

In section II we describe the thermodynamic model used to construct the free energy. As mentioned above, the electrostatic free energy is constructed following a recent approach developed to compute the number of condensed counterions in spherical ion penetrable spheres as a function of the nondensed (fractal) charge density from the center of mass,^{15a} with two slight but important modifications: (i) only the free counterions contribute to the screening involved in the Debye–Huckel electrostatic contribution to the free energy and (ii) the correlations between the condensed ions and the monomers induced by the electrostatic interactions are ignored (these correlations are the result of dipole–charge terms and higher order terms which are most important when the counterions have high valency^{15a} or when the linear charge density of the highly flexible chains is very high^{14,15a}). In section III we obtain numerical and analytical results for noncharged A block polydisperse micelles in nonpolar solvents, minimizing the free energy with respect to the corona radii $R_A(p)$. In section IV we analyze the results for the charged A block case. In the last section we summarize the results and discuss their relation to new experimental results.

II. Thermodynamic Approach

In this section we construct the free energy of M identical A–B diblock copolymer chains with $N = N_A + N_B$ monomers immersed in a solvent at temperature T with a bulk dielectric constant ϵ . Each chain has $N_B = (1 - f)N$ neutral nonsoluble monomers and $N_A = fN$ charged monomers, and the charge per monomer is $z_m = -1$. There are M_i^T counterions with valency $z_i = 1$. The solution must be electrically neutral,

$$MfNz_m + M_i^T z_i = 0 \quad (2)$$

so $M_i^T = MfN/P_z$, where $P_z = -z_i/z_m$, and it occupies a volume V . The total concentration of copolymer in the system is $\phi = MN/V$, and the concentration of copolymer aggregated with p chains is ϕ_p , such that

$$\phi = \sum_{p=1,2,\dots} \phi_p \quad (3)$$

Therefore, the number density of aggregates with p chains, n_p , is equal to ϕ_p/pN . As we discussed in the previous section, some of the small ions are confined, i.e., ‘condensed’, within a tube of radius $r_c \ll L_A = N_A a$, where L_A is the length of the tube and a is the size of each monomer. The condensed ions can move along the tube, and there is also the possibility of interchanging the condensed and free ions. We denote by $N_c(p)$ the average number of ions condensed on one p -aggregated chain. Therefore, the effective charge of a p -aggregate is

$$Z_p^{\text{eff}} = p z_m (fN - P_z N_c(p)) \quad (4a)$$

and the concentration of free, noncondensed, ions if $P_z = 1$ and $z_m = -1$ is

$$\phi_i^f = \sum_p n_p p (fN - N_c(p)) \quad (4b)$$

Each p -aggregate is contained within a sphere of average radius $R_p = R_A(p) + R_B(p)$ and volume $v_p = 4\pi R_p^3/3$. Since the cores are dense spheres with only B monomers,

$$R_B(p)^3 = a^3 p (1 - f)N \quad (5)$$

$R_A(p)$, on the other hand, is obtained by minimizing the free energy with respect to $R_A(p)$. We assume that the concentration of aggregates is very low, $\sum n_p v_p \ll 1$. Therefore the average distance between the aggregates is much larger than the maximum value of R_p . Furthermore, since the effective charge of the aggregates is strongly reduced by the condensed counterions, we neglect the interactions among the aggregates.

The free energy per unit volume of this system is given by the expression

$$F/V = F^0/V + F^f/V \quad (6)$$

where F^0 is the free energy of the system when $z_m = 0$ and F^f is the contribution to the free energy due to the charge of the A monomers and the free counterions. We construct F^0 using the simplest mean field theory that reproduces starlike micelle conformations,

$$F^0/V = F^{fp}/V + \sum_p n_p F_{\text{in}}(p) \quad (7)$$

where

$$F^{fp}/V = k_B T \sum_p n_p \ln \left(\frac{\lambda_p^3 \phi_p}{1 - \sum_p n_p v_p} \right) \quad (8)$$

corresponds to the translational free energy of the aggregates, λ_p being the appropriate thermal wavelength. Since the standard contribution from the entropy of mixing of the solvent at a concentration ϕ_s and the terms linear in n_p do not influence the numerical results, they are absorbed in the free energy reference

state on the left hand side of eq 6. The internal free energy of a p -aggregate $F_{in}(p)$ in eq 8 is given by

$$F_{in}(p) = F_p^{id} + F_p^{int} + F_p^{en} \quad (9)$$

where F_p^{id} is the free energy reduction of p chains with A and B blocks confined to $R_A(p)$ and $R_B(p)$, respectively, F_p^{int} is the interfacial energy between the B monomers and the water, and F_p^{en} is the interaction energy in the corona. We assume that the ideal free energy of the chain is given by¹⁶

$$F_p^{id} = k_B T_p \sum_{I=A,B} \left(\frac{3 \Delta R_I^2}{2 N_I a^2} + \frac{\pi^2 N_I a^2}{6 \Delta R_I^2} - 3.1449 \right) \quad (10)$$

where $\Delta R_I = 2R_I(p)$ is the end to end distance of the I block, $I = A, B$, and the interfacial energy is given by

$$F_p^{int} = k_B T 4\pi R_B^2 \gamma_{BS} \quad (11)$$

where γ_{BS} is the interfacial energy per unit area between the B monomers and the water. We include two-body interactions of strength $v = a^3(1 - 2\chi_{AS})$ where χ_{AS} is the net short range interaction per thermal energy between the A monomers and the water, and three-body interactions of strength $w = a^6$ in the interaction energy in the corona,

$$F_p^{en} = k_B T \left(\frac{v (pfN)^2}{2 R_A^3} + \frac{w (pfN)^3}{6 R_A^6} \right) \quad (12)$$

Notice that the internal free energy is constructed as a Flory free energy to avoid using a two-phase model which requires introduction of the solvent in the corona explicitly. Instead, the solvent entropy of mixing in the corona is introduced via the two- and three-body terms. When the free energy $F_{in}(p)$ is minimized with respect to $R_A(p)$, we recover eq 1a and 1b for \ominus solvents (setting $v = 0$ in eq 12) and good solvents (setting $v = a^3$ in eq 12), respectively.

The electrostatic contribution to the free energy in eq 6, F^c , contains the translation energy of the free ions F_f^{ti} , the electrostatic interactions among all the components (aggregates and free counterions), F^{el} , and the internal energy due to the charged components of the aggregates (the A monomers and condensed ions):

$$F^c/V = F_f^{ti}/V + F^{el}/V + \sum_p n_p F_{in}^c(p) \quad (13)$$

We use an ideal translation energy form,

$$F_f^{ti}/V = k_B T \phi_i^f \ln(\lambda_i^3 \phi_i^f) \quad (14)$$

where ϕ_i^f is given in eq 4b and λ_i is the thermal wavelength of free ions. The excluded volume of the free ions (M times the volume of the tube encasing each A block, $v_t = \pi r_c^2 f N a$, with $r_c \approx a$) was neglected in eq 14 because it is much smaller than V . The electrostatic interactions between the aggregates are neglected here because their effective charge is reduced by the condensed ions and their mass is much larger than that of the free ions, so only the Debye–Huckel energy term from the interactions among the free ions is included in F^{el} ,

$$F^{el}/V = - \frac{k_B T \kappa_f^3}{12\pi} \quad (15)$$

where κ_f^{-1} is the net Debye length determined by

$$\kappa_f^2 = 4\pi I_B \phi_i^f Z_i^2 \quad (16)$$

where $I_B \equiv \beta e^2/\epsilon$ is the Bjerrum length and $\beta \equiv 1/k_B T$. The last term of the free energy of eq 13 takes into account the internal free energy per aggregate due to the charge, $F_{in}^c(p)$, which includes the translation energy of the $N_c(p)$ condensed ions per chain along their confined volume v_t and the electrostatic interactions among charged monomers and condensed ions ΔF_p^{el} ,

$$F_{in}^c(p) = p K_B T N_c \ln(N_c/fN) + \Delta F_p^{el} \quad (17)$$

where the cube of the thermal length of the condensed ions is set equal to $\pi r_c^2 a$. In order to obtain an expression for ΔF_p^{el} , the internal excess free energy of the net polyion due to Coulombic interactions, we apply arguments similar to those used by P. Gonzalez-Mozuelos and M. Olvera de la Cruz.¹⁵ In principle, screened Coulombic interaction between a particle of species α and a particle of species γ inside the aggregate should be considered. However, κ_f^{-1} , the screening Debye length produced by the presence of the free ions in the vicinity of the aggregate, given by eq 16, is nearly zero in salt-free solutions. Therefore, the interactions between the α and γ particles separated by a distance r are approximated as

$$\beta u_{\alpha\gamma}(r) = z_\alpha z_\gamma \frac{I_B}{r} \quad (18)$$

The excess part of the free energy should include the interactions and correlations among the charge components of the aggregate that are not yet included in eq 9. In analogy to ref 15, we define the correlation functions¹⁷

$$c_{\alpha\gamma}(\mathbf{r}, \mathbf{s}) = - \frac{\beta \Delta F_p^{el}}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\gamma(\mathbf{s})} \quad (19)$$

where \mathbf{r} and \mathbf{s} are position vectors taken with respect to the center of the aggregate. Due to the spherical symmetry of the aggregate, these correlation functions should only depend on the radial distances $r = |\mathbf{r}|$ and $s = |\mathbf{s}|$ and the total distance $R = |\mathbf{r} - \mathbf{s}|$, so they are of the form $c_{\alpha\gamma}(r, s, R)$. The correlation functions defined in eq 19 have the same general properties as Ornstein–Zernike correlation functions. In particular, their asymptotic behavior in the limit of large values of R is also given by $c_{\alpha\gamma}(r, s, R) = -\beta u_{\alpha\gamma}(R)$, so we can write each correlation function as the sum of a long range term, given by the interparticle potential, plus a short range term ($c_{\alpha\gamma}^{sr}(r, s, R)$):

$$c_{\alpha\gamma}(r, s, R) = -\beta u_{\alpha\gamma}(R) + c_{\alpha\gamma}^{sr}(r, s, R) \quad (20)$$

If we neglect the short range correlation functions, which for $z_i = 1$ give only small corrections to the excess free energy ΔF_p^{el} , we obtain a mean field approximation,

$$\beta\Delta F_p^{\text{el}} \approx 4\pi^2 \sum_{\alpha} \sum_{\gamma} \int_0^{R(p)} dr r \rho_{\alpha}(r) \int_0^{R(p)} ds s p \gamma(s) \times \int_{|r-s|}^{r+s} dR R u_{\omega\gamma}(R) \quad (21)$$

$$\approx \frac{I_B}{R_A(p)} (Z_p^{\text{eff}})^2$$

where Z_p^{eff} is given in eq 4a. The level of approximation involved in eq 21 is consistent with the level of approximation used in F_p^{en} in eq 12. That is, if the potential $\beta u(r)$ is replaced by $v\delta(r)$, assuming that the distribution of monomers inside the globule is uniform, then the equivalent eq 21 is of the form $v(pfN)^2/R_A^3$, which is the two-body term in eq 12.

From now on throughout the paper we work in adimensional quantities obtained by multiplying F/V in eq 6 by βa^3 and dividing R_I by a for $I=A, B$. Therefore, n_p , ϕ_p , and ϕ are given in units of $1/a^3$, v in units of a^3 (throughout this paper v/a^3 is equal to 1 and 0 for good and Θ A solvents, respectively, and $w/a^6 = 1$), R_I and I_B in units of a , and γ_{BS} in units of $1/a^2$. In these units, for example, for diblocks of poly(ethylenepropylene) (PEP) and sodium poly(sterenesulfonate) (PSS) in water $\gamma_{BS} \approx 1.27$. The interfacial energy in this unit is given by $\gamma_{BS} 4\pi(R_B/a)^2 K_B T = \gamma^T S$, where S is the total surface, and for PEP in water $\gamma^T \approx 50$ dyn/cm² so $\gamma_{BS} = \gamma^T(3v/4\pi)^{2/3}\beta$, where $v = \text{mass/density} \approx 1.366 \times 10^{-22}$ cm³. The value of γ^T has been estimated following the Fowke's relation¹⁸ relating the water–air and PEP–air surface tensions to γ^T . For poly(*tert*-butylstyrene) (PtBS) the value of γ^T , estimated following the Fowke's relation, is also approximately 50 dyn/cm². Therefore, the γ_{BS} for the diblock copolymer PtBS–PSS in water is of the same order of magnitude as the one for PEP–PSS. Experimental studies on PtBS–PSS diblocks with f and N values close to the values used in the numerical solutions given in section IV were recently reported.¹⁹

The free energy is minimized when (i) the chemical potential of the chains in all the aggregates $p = 1, 2, \dots$ is equal to the chemical potential of the free chains ($p = 1$),

$$\mu_p/p = \mu_1 \quad (22a)$$

where $\mu_p = \partial(F/V)/\partial n_p$ (this condition is often rewritten as

$$\ln \phi_p = p \ln \phi_1 - \beta(\mu_p^{\circ} - p\mu_1^{\circ}) \quad (22b)$$

where μ_p° is the p -aggregate standard pseudochemical potential, the free energy difference per unit volume from adding an aggregate of size p to a pure solvent at a fixed position), (ii) the corona radius R_A takes its minimum value,

$$\partial(F/V)/\partial R_A = 0 \quad (23)$$

and (iii) the chemical potential of the free counterions is equal to the chemical potential of the condensed counterions for $p = 1, 2, 3, \dots$,

$$\partial(F/V)/\partial n_i = \partial(F/V)/\partial(n_p p N_c) \quad (24)$$

where the number density of free ions $n_i = \phi_i$ in our approach. The standard equal chemical potential equation (eq 22) is solved here for the first time by minimizing the free energy with respect to the corona radius (eq 23), which leads to

$$(fN - N_c)^2 I_B = (1/p)[12R_A^3/fN - \pi^2 fN/(12R_A) - 1.5vp(fN)^2/R_A^2 - p^2(fN)^3/R_A^5] \quad (25)$$

and simultaneously finding $N_c(p)$ from eq 24, which leads to

$$\ln(n_p fN/N_c) - I_B \kappa_f/2 = -(I_B p(fN - N_c)/R_A)[2 + \partial R_A/\partial N_c(fN - N_c)/R_A] \quad (26)$$

From these two last equations one can obtain two limiting R_A scaling regimes depending on the value of p . For $p \gg 1$ eq 25 gives $(fN - N_c(p)) \approx 0$, giving the same result for R_A as eqs 1, as expected because the micelles must be nearly neutral in this limit. For smaller p values, however, eq 25 gives $R_A(p) \approx (I_B p fN/3)^{1/3}(fN - N_c(p))^{2/3}$, for which, in order to satisfy eq 26, $(fN - N_c(p)) \approx fN/(I_B p)^2$, giving $R_A \approx fN/(I_B p)$. In section IV these results are obtained by solving numerically eqs 22–24. We also compute p_{max} , the value at which n_p versus p is maximum, and p^* , defined by

$$[\partial(E/p)/\partial p]_{p^*} = 0 \quad (27)$$

where $E/p = (1/p)(\mu_p^{\circ} - p\mu_1^{\circ})$. The degree of polydispersity is evaluated by computing the number average, $\langle p \rangle_n$, the weight average, $\langle p \rangle_w$, the z average, $\langle p \rangle_z$, and the $z + 1$ average, $\langle p \rangle_{z+1}$, defined as

$$\langle p \rangle_n = M_1/M_0 \quad (28a)$$

$$\langle p \rangle_w = M_2/M_1 \quad (28b)$$

$$\langle p \rangle_z = M_3/M_2 \quad (28c)$$

$$\langle p \rangle_{z+1} = M_4/M_3 \quad (28d)$$

where

$$M_i = \sum_{p=1,2,\dots} p^i n_p \quad (29)$$

The moments $\langle p \rangle_n$ and $\langle p \rangle_w$ are accessible by osmotic measurements and by light scattering, respectively. The critical micelle concentration (cmc) is the copolymer concentration at which

$$\ln n_p = \ln n_1 \quad \text{at} \quad p = p_{\text{max}} \quad (30)$$

In all the figures in this paper we show numerical results for $\gamma_{BS} = 1.27$, $N_A = 400$, and $N_B = 25$. In the figures for nonpolar solvents $I_B = 0$ and for polar solvents $I_B = 2.8$. Notice that since I_B is really I_B/a , the value 2.8 is for fully charged PSS. Also, $\gamma_{BS} = 1.27$ is roughly for PEP, as explained above. Though much larger values of γ_{BS} change the results obtained in this paper, they are unphysical (they will be discussed in the last section of the paper).

III. Micelles in Nonpolar Solvents (Noncharged A-Block)

In Figure 1 we show the variation of the concentration of free chains as a function of the total concentration of copolymers, $\ln \phi_1$ versus $\ln \phi$, for A-good solvents (a similar curve is obtained for A- Θ solvents with smaller cmc and $\ln \phi_1$ values because more chains aggregate in A- Θ solvents). In Figure 2 we plot $\ln n_p$ versus p and show the cmc computed using eq 30, and in Figure 3 we show the degree of polydispersity by plotting the

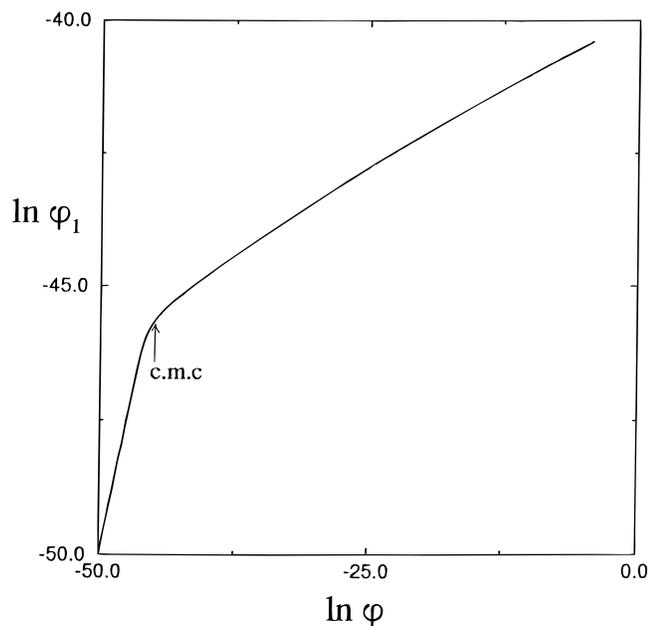


Figure 1. Logarithm of the concentration of free chains ($\ln \phi_1$) versus the logarithm of the total concentration of diblock copolymer chains ($\ln \phi$) in nonpolar good solvents for the A-blocks. The parameters are $N_A = 400$, $N_B = 25$, $l_B = 0$, $\nu = 1$, and $\gamma_{BS} = 1.27$.

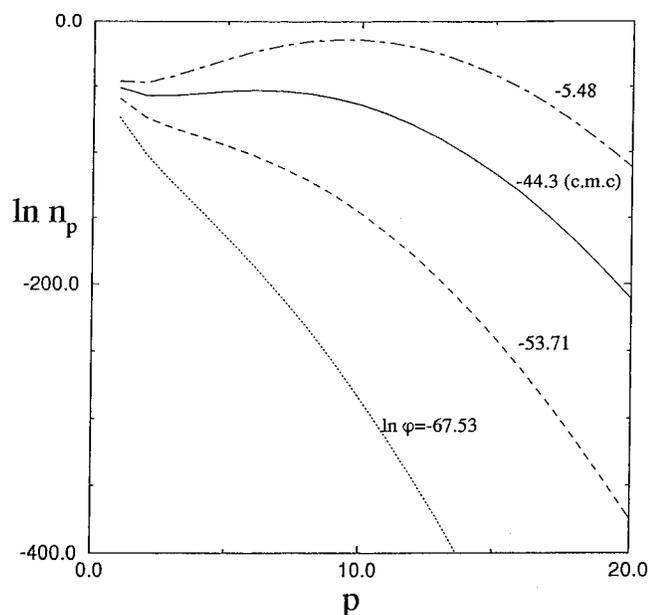


Figure 2. Number of aggregated chains with p chains ($\ln n_p$) versus p for systems described in Figure 1.

moments defined in eqs 28 for A-good solvents. Micelles of uncharged A-blocks are monodisperse, and the degree of polydispersity decreases as p_{\max} (γ_{BS} and/or N) increases.

Analytical results can be easily obtained for uncharged micelles. For example, from eq 23 we recover eqs 1, and from eq 27 we obtain

$$p^* \approx ((1 - f)N)^{0.8} \gamma_{BS}^{1.2} \quad (31)$$

for an A- Θ solvent, and

$$p^* \approx (1 - f)^{10/11} f^{-3/11} N^{7/11} \gamma_{BS}^{15/11} \quad (32)$$

for an A-good solvent. The values for $R_A(p^*)$ and $R_B(p^*)$ are obtained setting $p = p^*$ in eqs 1. The numerical

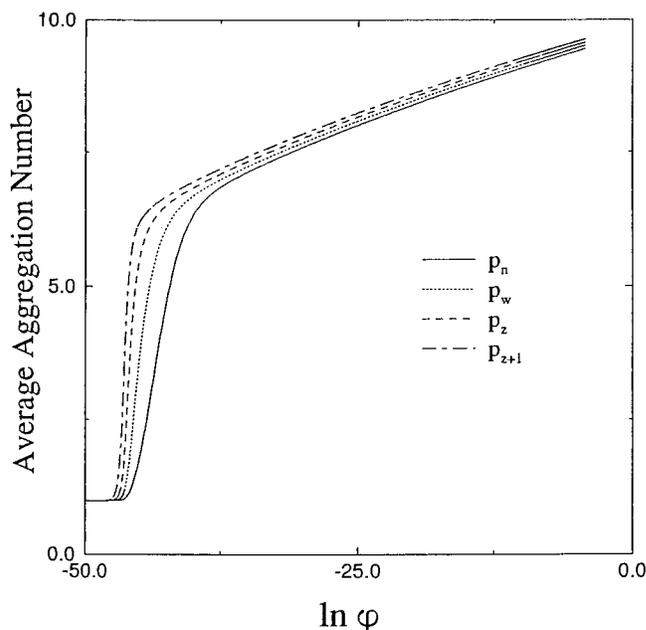


Figure 3. Average aggregation number versus the logarithm of the concentration of chains for systems described in Figure 1.

solution of eqs 23 and 27 for $N \in [400, 1500]$, $f \in [0.1, 0.9]$, and $\gamma_{BS} \in [0.5, 20]$ above the cmc leads to $p^* \approx N^\alpha \gamma_{BS}^\delta$ with $\alpha \in [0.87, 0.92]$ and $\delta \in [1.09, 1.1]$ for an A- Θ solvent and $\alpha \in [0.74, 0.84]$ and $\delta \in [1.19, 1.22]$ for an A-good solvent. The variations are due to the sensitivity of p^* to the value of γ_{BS} . At the cmc, p_{\max} computed solving eqs 22 and 23 is smaller than p^* , but as the concentration of copolymer increases, p_{\max} approaches p^* .

IV. Micelles in Polar Solvents (Charged A-block)

We solved numerically eqs 22–24 using the same parameters as in Figures 1–3 from the previous section, but with $l_B = 2.8$. The most spectacular difference between uncharged and charged systems is the fact that in charged systems the fraction of free chains above the cmc decreases as the concentration of copolymer increases, as shown in Figure 4a for A-good solvents and in Figure 4b for an A- Θ solvent. While in uncharged A-blocks always $\ln \phi_1$ in A- Θ solvents is lower than that in A-good solvents, in charged A-blocks this is only true below the cmc. For copolymer concentrations above the cmc, the concentration of free chains in A-good solvents is lower than that in A- Θ solvents, contrary to the case for uncharged chains. In Figure 5a and b we plot the $\ln n_p$ versus p and show the cmc given by eq 30 for A-good and A- Θ solvents, respectively. The cmc for charged systems is larger than the cmc of uncharged systems. However, while in uncharged systems the cmc for A- Θ solvents is less than that in A-good solvents, in charged systems, unless γ_{BS} is very large, it is the opposite. Since the population of large micelles is very low in charged systems above the cmc, p_{\max} in charged systems is smaller than that in uncharged systems. Also, contrary to the case for uncharged systems, in charged systems p_{\max} is almost constant above the cmc and it does not approach p^* . Therefore, for charged systems a monodisperse model with p^* given as a characteristic aggregation number has no significance. Charged systems have large deviations between $\langle p \rangle_n$ and $\langle p \rangle_w$, as shown in Figure 6a and b for A-good and A- Θ solvents, respectively.

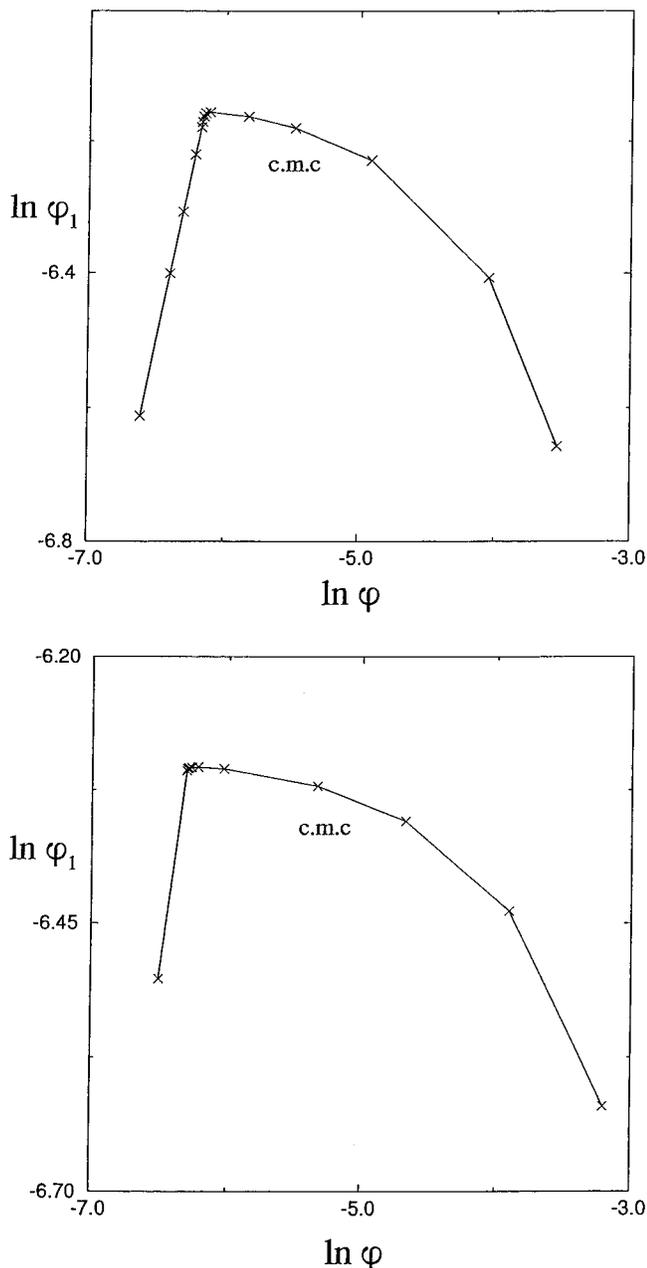


Figure 4. (a) Logarithm of the concentration of free chains ($\ln \phi_1$) versus the logarithm of the total concentration of diblock copolymer chains ($\ln \phi$) in (a) polar good solvents ($v = 1$) and (b) polar Θ solvents ($v = 0$) for the A-blocks. The parameters are $N_A = 400$, $N_B = 25$, $l_B = 2.8$, and $\gamma_{BS} = 1.27$.

As previously stated, the number of condensed counterions per chain in a p -aggregate, $N_c(p)$, tends to fN when $p \gg 1$, as shown in Figure 7a for A-good solvents. That is, large micelles are indeed nearly neutral. The scaling of their radii, $R_A(p)$, tends to the scaling of neutral micelles, given in eq 1, as shown in Figure 7b. The population of large micelles, however, is zero, as can be seen in Figure 5a. Notice in Figure 7 that, above the cmc, $N_c(p)$ and the scaling of $R_A(p)$ are independent of the total concentration of copolymer, ϕ . This may explain why p_{\max} is ϕ independent above the cmc. Above the cmc, $p_{\max} = 7$ for the systems described in Figure 7, and the concentration of copolymer aggregated with p chains, $\phi_p = pNn_p$, for $p = p_{\max}$ is approximately 0.002 at the cmc and 0.015 at $\phi = 0.01747$. For p values around p_{\max} the scaling of R_A with p is $1/p$ for A-good and A- Θ solvents, as predicted in the previous section

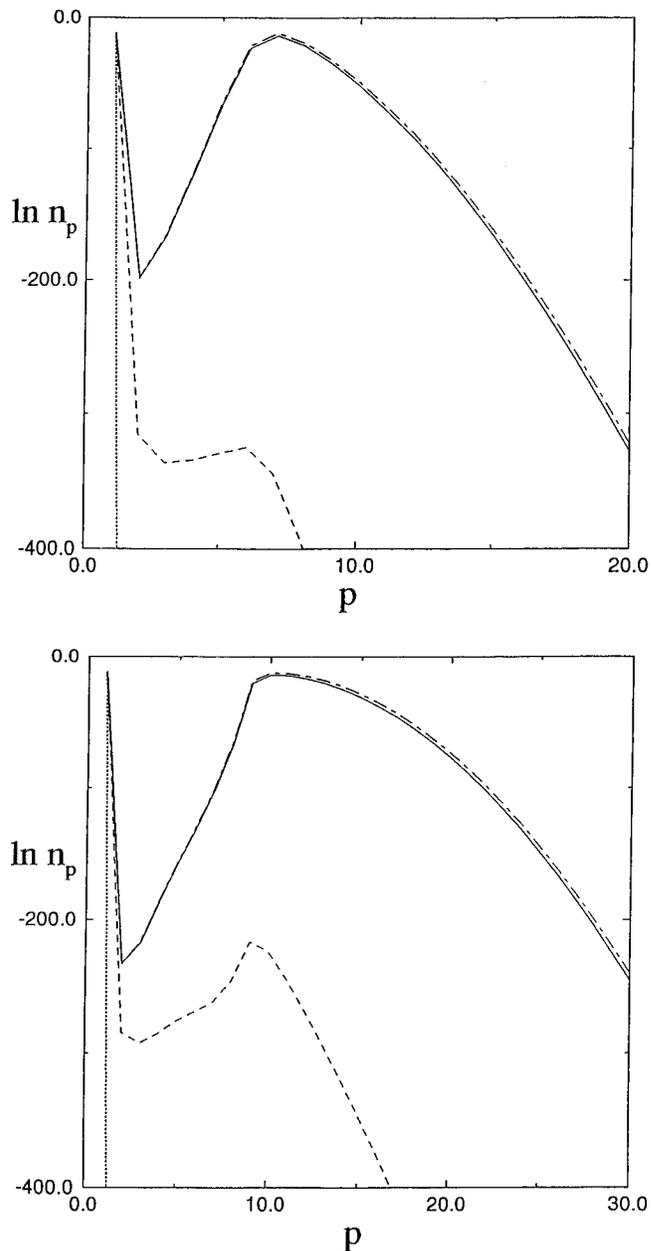


Figure 5. (a) The number of aggregated chains with p chains ($\ln n_p$) versus p for systems described (a) in Figure 4a with $\phi = 0.00011$ (dotted line), $\phi = 0.00134$ (dashed line), $\phi = 0.00415 = \text{cmc}$ (solid line), and $\phi = 0.01747$ (solid-dashed line) and (b) in Figure 4b with $\phi = 0.00011$ (dotted line), $\phi = 0.0015$ (dashed line), $\phi = 0.00483 = \text{cmc}$ (solid line), and $\phi = 0.02012$ (solid-dashed line).

for charged micelles with a small number of aggregated chains.

V. Discussion and Conclusions

Micelles are predicted in A-B block copolymers with hydrophobic B blocks and charged A blocks in salt-free aqueous solutions using a simple thermodynamic model for polydisperse micellar suspensions which includes ion condensation. We compare our results to those for uncharged A-block micellar suspensions. Uncharged A-block micelles are monodisperse, and p_{\max} tends to p^* (defined in eq 27) as the copolymer concentration increases above the cmc. Charged A-block micelles, however, are polydisperse and p_{\max} does not approach p^* above the cmc. The cmc in charged micelles when γ_{BS} is small is larger in A- Θ solvents than in A-good

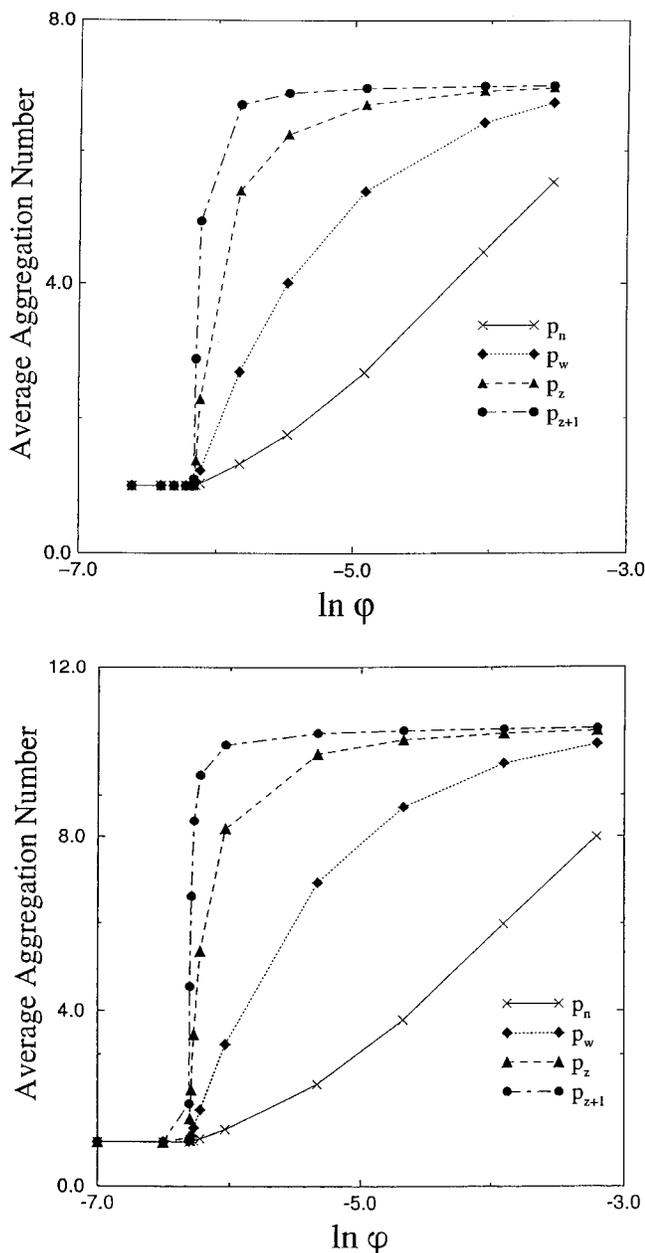


Figure 6. Average aggregation number versus the logarithm of the concentration of chains for systems described in Figure 4a and b.

solvents. Uncharged systems or charged systems with large γ_{BS} have smaller cmc values in A- Θ solvents. In charged systems above the cmc the fraction of free chains *decreases* as the concentration of copolymer increases, and it is smaller in A-good solvents than in A- Θ solvents, contrary to the case for uncharged suspensions. This is the most striking difference between charged and uncharged A block micellar suspensions.

Charged and uncharged A block micellar suspensions have common characteristics. As γ_{BS} increases and/or as $f = N_A/N$ decreases, p_{\max} (and p^*) increase and the cmc decreases. Also, in both suspensions the cmc and p_{\max} (and p^*) decrease as N decreases, and p_{\max} (and p^*) and the degree of polydispersity for A- Θ solvents is larger than that for A-good solvents. Charged systems, however, have smaller p_{\max} values and larger cmc values. Furthermore, in uncharged systems $R_A(p)$ is given by eqs 1 and p_{\max} , which tends to p^* , has a well-defined scaling with N and γ_{BS} . Therefore, in uncharged systems it is possible to know the scaling for the size of

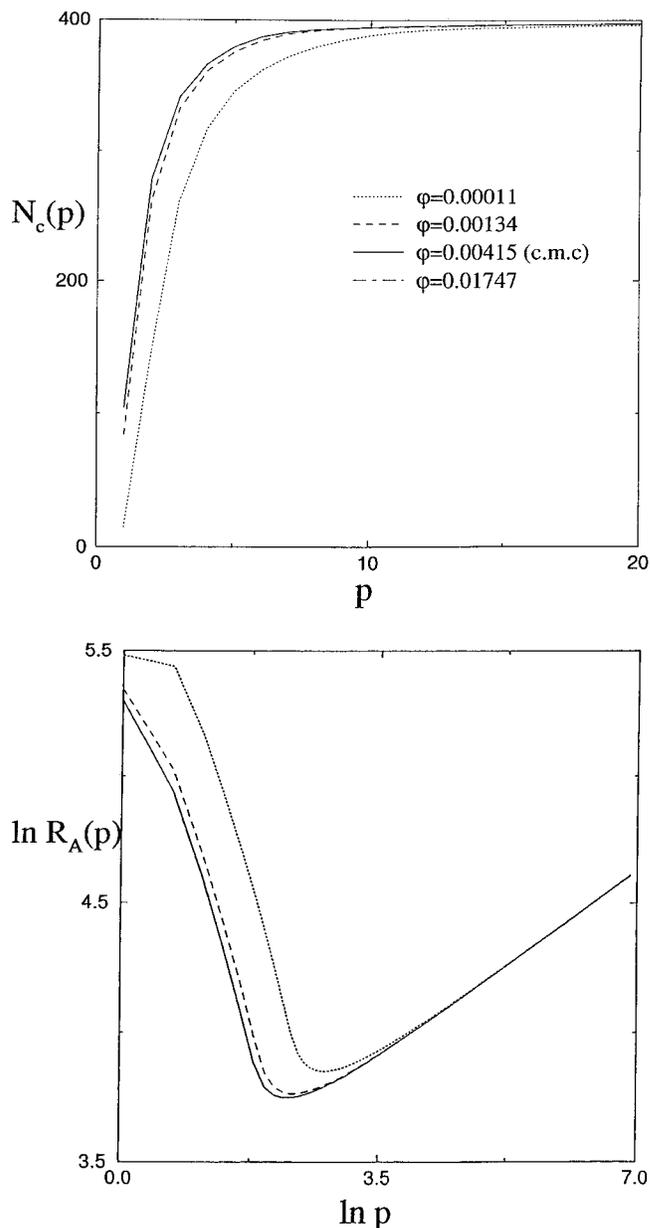


Figure 7. (a) Number of condensed counterions per chain in a p -aggregate ($N_c(p)$) versus p for systems described in Figure 4a. $N_c(p)$ values for $\phi = 0.00415 = \text{cmc}$ and $\phi = 0.01747$ are nearly identical. (b) Logarithm of the radius of the corona of a p -aggregate ($R_A(p)$) versus the logarithm of p for systems described in part a. $\ln R_A(p)$ values for $\phi = 0.00415 = \text{cmc}$ and $\phi = 0.01747$ are nearly identical.

the most populated (p_{\max}) micelles. In charged systems, however, $R_A(p)$ has various scaling regimes: stretched charged chain scaling for p very small ($R_A \approx N/p$) and uncharged chain scaling for $p \gg 1$ (given by eqs 1). In charged systems one cannot obtain scaling forms for p^* (which is useless in charged systems) nor for p_{\max} ; their scaling is very sensitive to the numerical values of γ_{BS} and l_B/a . One can conclude simply that, for experimentally accessible γ_{BS} and N values, such as the numerical values used here, p_{\max} for fully charged chains is small. Therefore, the chains in the most populated micelles are stretched.

The existence of such micelles is confirmed by light, neutron, and X-ray scattering.^{10,19} Furthermore, a rather large polydispersity was found, like theory predicts in some range of concentrations. Special care has to be taken, however, to remove the influence of scarce big aggregates,¹⁰ whose effect is only sensible at

low angles of scattering (for light), and deduce the true polydispersity of micelles for comparison with theory. The existence and state of equilibrium of these aggregates is still a matter of debate, since they do not seem to be described by our current theory. Other groups have reported analogous behaviors (see ref 20, for instance). The measured average aggregation number for the copolymer PtBS-PSSNa is on the order of 30 as measured by both light and neutron scattering. This is in excellent agreement with theory, which gives p_w of order 26 for γ_{BS} equal to 2.3, a reasonable theoretical estimation of the surface tension. At last, the radius of gyration of the micelles can be compared to the R_A value of the micelles given by theory. As shown in Figure 6b, the polydispersity becomes very low for concentrations well beyond the cmc, where light-scattering measurements were performed. We can thus directly compare R_A to R_g , the radius of gyration, by taking into account the numerical factor linking these two quantities for a star. This factor is not known with certainty, since it depends on the statistics of the chain. For a single chain it is found that $R_g = 2R_A/12^{1/2}$ for a rod and $R_g = 2R_A/6^{1/2}$ for a Gaussian chain. For stars, experiments on neutral stars show that the gyration radius of the star is roughly twice the gyration radius of a single chain whose star is made of p elements. We thus find that the experimental R_g (found to be on the order of 60 nm) should lie in between $4R_A/12^{1/2}$ and $4R_A/6^{1/2}$, where R_A is taken for the value of the aggregation number p_{max} , which leads to an interval of 9.9–14 nm. The discrepancy between theory and experiments can have a twofold origin: (1) experiments are never in a range where polydispersity seems negligible (see above) and (2) theory does not allow for an inner concentration of the noncondensed ions which is different from the outer one. Such an osmotic pressure could be responsible for an additional stretching of the arms.

It is important to point out that, for very large values of γ_{BS} and l_B/a , the theory predicts very large p_{max} ,

leading to neutral chain scaling (given in eqs 1) for the chains in the most populated micelles.

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