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Hydrophobic-Charged Block Copolymer Micelles Induced by Oppositely Charged Surfaces: Salt and pH Dependence

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ABSTRACT: We analyze the possibility of inducing surface micellization of hydrophobic and charged block copolymers by an oppositely charged surface using a two-state model with lateral correlations among adsorbed chains. The electrostatic attraction between the charged block and the charged surface induces diblock copolymer micellization on the surface at copolymer concentrations well below the critical micelle concentration in the bulk. We study systems with strong charge groups which have fixed charge densities and systems with weak charge groups which have solution-dependent degrees of ionizations. We analyze the effects of salt concentration, solution pH, surface charge density, polyelectrolyte block line charge density, surface tension of the hydrophobic block, and polymerization degrees of the blocks on the induced micellization. It is found that at low salt concentrations the number of chains per micelle does not significantly depend on the degree of polymerization of the charged block. The addition of salt increases the critical surface micelle concentration when the electrostatic attraction between the charged blocks and the surface dominates the electrostatic repulsion among adsorbed chains. At low salt concentration, the excluded volume has a minor effect on surface induced micelles for systems with strong charge groups. However, in systems with weak charge groups, where both the surface and block degrees of ionizations are determined self-consistently as a function of pH, the excluded volume decreases the pH effect on the polyelectrolyte degree of ionization at surfaces.

I. Introduction

Molecular self-assembly is a growing challenging field.[1−5] To further advance this field, it is important to learn how to self-assemble structures at special regions in a system and how to tune the structure without using extra facilities or further chemical modification of the components. In this paper, we study the possibility of inducing surface micelles of hydrophobic-charged copolymers in the presence of an oppositely charged surface by modifying the salt concentration and pH value in solutions.

Diblock copolymers made of one charged block and one hydrophobic block form micelles in aqueous solutions. These micelles have been extensively studied experimentally[6−10] and theoretically.[11−17] The research interest is driven by large potential applications including drug delivery.[18,19] In solutions, when the copolymer concentration exceeds the critical micelle concentration (cmc), hydrophobic blocks of different chains self-assemble into micelle cores. The self-assembled structure is controlled by the structure of the copolymer itself and the competition among interfacial energy of the core−water interface, the electrostatic energy of the charged blocks, and the entropic contribution to the free energy.

Uncharged diblock copolymers form micelles in selective solvents.[20−23] Micelles can form on a surface even when the bulk copolymer concentration is less than cmc if there is an attraction between the surface and one of the two blocks. Indeed, short-range attraction between the surface and the solvent unfavorable block induces surface copolymer micellization, a process that has been studied analytically[24] as well as been experimentally confirmed.[25]

A charged surface has the possibility to induce surface self-organization of charged−neutral block copolymers. This case is relevant to understanding biological phenomena, which involve electrostatic interactions and short-range or specific interactions. Self-assembly induced by a charged surface is also a powerful method for material scientists to fabricate complex structures at certain positions in a system. In nature there are two main types of charge groups: strong charge groups such as phosphate and sulfonate groups and weak charge groups such as carboxyl and aniline groups. The assembled structure of system with strong charge groups might be manipulated by controlling electrostatic interactions through varying solution ionic strength. For systems with weak charge groups, the solution pH value affects the ionization of acid groups and the association of base groups with hydrogen ions. Therefore, the surface and polyelectrolyte charge densities can be effectively tuned by means of pH variation in experiments to induce or suppress assembly. Generally, the charges of all chemical groups are related to the hydrogen ion concentration. Notice that systems with strong charge groups are only special situations of systems with weak charge groups. For example, though at physiological pH conditions and within a large range of pH values phosphate groups have pH-independent charge, the ionizations of these groups are affected by pH when the pH is less than two. It is important to analyze the properties of systems with weak charge groups because the degree of ionization depends on the local environment (the charges around the weak charge groups) and has to be determined self-consistently. This approach is different from systems with strong charge groups. In this paper, we analyze micellization in systems with strong charge groups, sometimes denoted as fully or strongly charged system, and in systems with weak charge groups, sometimes denoted as partially or weakly charged systems.

Charged surface induced cationic surfactant micellization has been studied experimentally.[26,27] However, we are not aware of any experimental or numerical papers reporting charged surface induced polyelectrolyte diblock copolymer micellization. Surface induced micellization in uncharged copolymer and

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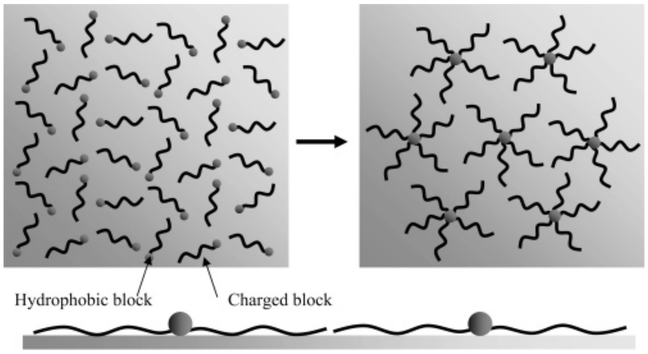

Figure 1. Schematic sketch of diblock copolymer micelles on a charged surface.

surface systems has been analyzed by accounting the interaction among one micelle and the surface.[24] However, in charged systems lateral correlations among micelles due to long-range electrostatic interactions have to be included and determined self-consistently. These lateral correlations restrict the density fluctuations of the adsorbed copolymers, resulting in different distributions of micelles on the surface to that on an uncharged surface. When polyions adsorb on charged surfaces, these correlations dominate the degree of adsorption, invalidating the mean-field Poisson−Boltzmann approach,[28] which determines the adsorption profile perpendicular to the surface and therefore ignores all the lateral correlations. At low salt concentration, these lateral correlations lead to nearly monodisperse surface micelles with surface distributions comparable to those found in the adsorption of multivalent particles on oppositely charged surfaces described by two-dimensional Wigner cells.[29−31] We follow a similar description here to analyze oppositely charged surface induced micellization of hydrophobic-charged copolymer chains. In this case, there is a competition between short-range attractions of hydrophobic blocks and long-range net electrostatic repulsions among charged blocks. Systems with competing short- and long-range interactions give rise to nearly periodic surface charged patterns,[32−34] which can be described by Wigner cells and/or Ewald sum techniques.[32] In bulk micellization of charged copolymers, the concentration of free chains decreases rapidly when the copolymer concentration is higher than the critical micelle concentration,[12] and the micelles forming three-dimensional Wigner cells have a narrow aggregation number distribution;[35] this is in contrast to bulk neutral micelles where there is always a coexistence of free chains and chains in micelles. In charged surface induced micellization, since the concentration of micelles on the surface is large, the micelles are expected to be strongly correlated laterally and therefore monodisperse, as shown in Figure 1. Therefore, we cannot use the Poisson−Boltzmann approach and instead use a Wigner-Seitz cell model in two dimensions to obtain the degree of adsorption and the structure of the micelles self-consistently, as discussed in section II.

We study here the correlated regime applicable at low ionic strength conditions because we are interested in describing the possibility of inducing micellization on surfaces when the bulk concentration is well below the cmc. In the limit of large ionic strengths, charged copolymer can easily form micelles in a bulk solution because the electrostatic repulsion is effectively screened by a large amount of salt. Therefore, we do not consider high salt concentrations in our approach. Though we include the macroion adsorption in a nonlinear way and short-range lateral correlations, the free salt ions are included using a Debye−Hückel approach. This works when the surface charge is nearly compensated by the adsorbed chains and there is no much charge inversion.[29,30] In the case of large surface charge inversion one has to include the salt ions explicitly in a nonlinear way and short-range correlations, for example, by including ion condensation along the adsorbed chains.[36]

The goal of our work is to construct a reasonable model for understanding the effects of surface charge density, polyelectrolyte block line charge density, surface tension of the hydrophobic blocks, salt concentration, excluded volume, degrees of polymerization of the blocks, and the pH value on charged surface induced micellization. The paper is organized as follows. In section II we describe the theoretical model of charged surface induced micellization for systems with strong charge groups and the results. System with weak charge groups are studied in section III. The conclusions are summarized in section IV.

II. System with Strong Charge Groups

The charges of strong charge groups are nearly independent of the solution pH value. In this section we assume all the charges have a fixed value.

A. Model of Surface Micellization. We consider a solution of charged block copolymers at a concentration less than the bulk cmc. Each copolymer comprises a flexible polyelectrolyte A block with a degree of polymerization N_A in which the fraction of charged monomers is f and a hydrophobic B block with a degree of polymerization N_B. In bulk solutions, spherical micelles are expected to form in the case of highly asymmetric copolymers ($N_A \gg N_B$). Therefore, our adsorbed micelles are expected to be circular micelles. The hydrophobic B blocks form a spherical core with no water molecules inside due to the large surface tension, γ. The spherical core of the B blocks is extruded from the charged surface because of the large interfacial tensions of the A−B interface and of the B−water interface; that is, we are considering a highly hydrophilic surface such that the contact angle between the hydrophobic core of the B blocks and the surface is close to 180°, as shown in Figure 1. The surface has a homogeneous charge distribution of charge density σ. For simplicity, the permittivity of the substrate is assumed to be equal to the permittivity of the water to neglect the image charge effect. If the substrate dielectric constant is much lower than that of water, the total effect is equivalent to assuming an image charge of the same sign of the adsorbed charge at the other side of the substrate, and this leads to an effective decrease of the adsorption.[37] For the charge densities of the adsorbed chains used here the results will be equivalent to considering adsorption to surfaces with weaker charge density in a media with equal dielectric constant.

In our model, we also presume that the nonelectrostatic, short-range interaction between the charged surface and water is identical to that of A block and water. We discuss the effect of this approximation in our results in section II.B.

The degree of polydispersity of surface micelles is expected to be narrow at low salt concentrations because the micelles interact with each other via a long-range potential on the surface. The density fluctuations are suppressed by the correlation hole effect.[31,38,39] The physical implication is that there is a Wigner-Seitz cell of radius R determined by the surface charge density and the repulsion between charged micelles or single chains before the micellization on the surface; that is, there are strong lateral correlations among highly charged particles adsorbed on oppositely charged surfaces.[28] Since the Wigner-Seitz cell is repeated on the surface, it is not possible to have coexistence of free adsorbed charged chains and charged micelles on oppositely charged surfaces in the low salt limit, as we show in section II.B by assuming two populations of adsorbed chains (single and aggregated) and finding solutions only for the case when they are all free or all aggregated. That is, there is no coexistence of free and aggregated chains on the surface, and this also suggests that the micelles are monodisperse because of the strong lateral correlations. This is in contrast with uncharged systems, where the micelles and single chains may coexist on a surface due to entropic contributions.[23]

There are two conditions studied here for micelles on a surface. One is the dilute surface adsorption regime when the micelles are clearly not overlapping. In this case the radius of a single chain or micelle on the surface, L_s, is smaller than the size of Wigner-Seitz cell, R. The second case is at the contact condition, $L_s = R > N_A^{1/2}a$, at which the chains are on average touching each other and forming a uniform layer. We use a two-state model to determine the conditions at which the different regimes apply and resolve the physical properties of the system. The two-state model counts the entropic and energetic contributions to the free energy from all the chemical components in two states: adsorbed and in the bulk. Thermodynamic equilibrium among the components in the two states is ensured by equating their chemical potentials, which is equivalent to minimizing the total free energy. This method is extensively used in multicomponent solutions to determine the degree of adsorption of different components at interfaces.[40] It has been used to determine the degree of ion association along polyions in aqueous solutions. The model has been applied to various geometries including charged colloids,[41,42] infinite rods,[43] and finite charged chains with different fractal properties.[44,45] In all of the above examples the results have been shown to be equivalent to the solution of the nonlinear Poisson−Boltzmann equations when short-range correlations are ignored and have the advantage to be able to include short-range correlations. The two-state model is also very useful to describe adsorption of multivalent ions to an oppositely charged surface when short-range correlations are significant. The two-state model has been applied to study the condensation of divalent ions on oppositely charged surfaces.[46] The model was shown to be equivalent to a modified one-dimensional nonlinear Poisson−Boltzmann approach that includes short-range correlations, termed the site-binding model.[47] The site-binding model is extensively used to describe the effect of short-range interactions among adsorbed divalent ions and the surface. The full three-dimensional Poisson−Boltzmann approach including lateral correlations among adsorbed macroions with simple structure functions has been resolved numerically in simple systems.[48] The two-state model can easily incorporate the correlation and other effects for complicated systems, providing a convenient method to study polymer adsorption and assembly.[36] We describe the two-state model for induced micellization in the following paragraphs.

For the condition of $L_s < R$ the total free energy (in the units of k_BT) of the system can be written as

$$F = F_s^{m} + F_s^{ea} + F_s^{er} + F_b^{c} \tag{1}$$

The first term in eq 1 is the free energy of micelles on a charged surface, which includes four terms:

$$F_s^{m} = F_s^{ms} + F_s^{mel} + F_s^{mc} + F_s^{mex} \tag{2}$$

The surface interfacial energy of the core−water interface is given by

$$F_s^{ms} = \frac{S}{\pi R^2}\gamma A \tag{3}$$

where S is the area of the charged surface and $S/\pi R^2$ is the number of micelles or single chains adsorbed on a surface. The area of the micelle core, A, is equal to $4\pi R_{core}^2$, where R_{core} can be obtained by

$$\frac{4}{3}\pi R_{core}^{\ 3} = pN_Bb^3 \tag{4}$$

Here p is the number of chains in one micelle (p is one for single chains) or aggregation number. The size of the B monomer is b.

The second term F_s^{mel} is the intramicelle or single chain electrostatic repulsion[49]

$$F_s^{mel} = \frac{S}{\pi R^2}\frac{l_B(pN_Af)^2}{L_s} \tag{5}$$

in which l_B, Bjerrum length, is equal to $e^2/\epsilon k_BT$, where e is the elementary charge, ϵ is the solvent permittivity, and k_BT is the thermal energy. Equation 5 is a good approximation at low salt concentration when the Debye screening length is larger than L_s. The dependence of bulk cmc on the salt concentration was studied by Borisov et al. for different conditions.[13] They found bulk critical salt concentrations for different conditions. Since we are only interested in surface induced micellization below the bulk cmc, salt concentrations in our study are below these bulk critical salt concentrations.

The free energy contribution due to the flexible chain extension in the lateral direction and chain confinement in the direction normal to the surface, F_s^{mc}, is given by[12,50]

$$F_s^{mc} = \frac{S}{\pi R^2}p\left(\frac{3L_s^{\ 2}}{2N_Aa^2} + \frac{\pi^2}{6}\frac{N_Aa^2}{D^2}\right) \tag{6}$$

Here a is the monomer size of A block and D is the thickness of adsorbed A block.

The last term in eq 2 results from the excluded-volume effect

$$F_s^{mex} = \frac{S}{\pi R^2}\frac{\upsilon}{2}\frac{(pN_A)}{\pi L_s^{\ 2}D} \tag{7}$$

where υ is the second virial coefficient and is equal to $a^3(1 - 2\chi)$, and χ is the Flory−Huggins interaction which is positive if the short-range interactions are only van der Waals interaction and is assume to be less than $^1/_2$ in our studies. At low salt concentrations, the copolymer fluctuations on the surface are negligible when R is much less than $N_A^2f^2l_B$; that is, the electrostatic interactions between neighboring chains are much larger than k_BT, leading to strong lateral correlations between adsorbed chains.

The electrostatic attraction energy between the charged A blocks and the oppositely charged surface, F_s^{ea}, can be written as[37]

$$F_s^{ea} = -\frac{S}{\pi R^2}\frac{4\pi l_B\sigma pN_Af(1 - \exp(-D\kappa))}{D\kappa^2} \tag{8}$$

by assuming the A blocks have a homogeneous vertical density distribution. In eq 8, κ^{-1} is the Debye screening length given by $\kappa^2 = 8\pi l_B c$, in which c is the salt concentration. For our considered low salt concentration regime, $D\kappa$ is much less than 1. Therefore, eq 8 is approximately equal to $-(S/\pi R^2)pN_A f\Psi$, where $\Psi = 4\pi l_B \sigma \kappa^{-1}$ is the surface potential. Another approximation method to calculate the electrostatic attraction among the adsorbed chain and the surface is to assume that the center of mass of the adsorbed chains is located at distance $D/2$ normal to the surface. The two methods have the same results for the condition of $D\kappa$ is much less than 1 studied here.

The electrostatic repulsion energy between micelles or single chains on the surface is computed by assuming a uniform charge distribution in the Wigner-Seitz cell

$$F_s^{er} = \frac{S}{\pi R^2}\left[\frac{(pN_A f)^2}{\pi R^2}\frac{\pi l_B}{D^2\kappa^3}(\exp(-2D\kappa) - 1 + 2D\kappa) - \frac{(pN_A f)^2 l_B}{R}\right] \tag{9}$$

The calculation is based on the assumption that the adsorbed layer is composed by segregated disks. The first term in the brackets comes from the interaction between one uniformly charged disk and a charged layer of thickness D.[37] The second term results from the self-energy of the disk interacting with itself, which is included in the first term via the layer potential. Equations 8 and 9 are obtained using the Debye−Hückel approximation which is valid when the electrostatic interaction, u, between one ion on the surface and the surface-layer structure, is less than k_BT, that is, $u/k_BT = 4\pi l_B\kappa^{-1}(\sigma - pN_A f/\pi R^2) < 1$. This provides the low salt concentration limit of applicability of our model, which is easy to be satisfied even at low salt concentration (κ^{-1} is large) for large N, because in this case the second term ($\sigma - pN_A f/\pi R^2$) is small due to the release of the counterions upon copolymer adsorption. Since we are only interested in surface induced micellization below the bulk cmc, the high salt concentration limit of our model is given by ref 13 where the bulk cmc is obtained. Equation 9 is for the condition of L_s is close to R. When $L_s \ll R$, the following equation should be used.[51]

$$F_s^{er} \approx \frac{S}{\pi R^2}\, 2\frac{l_B(pfN)^2}{R^2\kappa}\exp(-\kappa R) \tag{10}$$

We compare the results of these two approximations in section II.B.

In eq 1, the last term is the free energy contribution from the bulk. Since we only consider solutions with copolymer concentrations less than the cmc, then we presume all the chains in the bulk solution are single chains. In the previous model of short-range interaction induced neutral copolymer surface micellization,[24] the bulk solution is treated as a reservoir (grand canonical approach). For strongly charged polyelectrolytes where ion condensation is important, and/or to study pH effects, it is more convenient to use our canonical free energy than the grand canonical approach. The free energy contribution of the bulk solution is composed of four terms:

$$\frac{F_b^c}{V} = \frac{\phi^m}{N_A}\left(\gamma A' + \frac{l_B N_A^{\,2} f^2}{L_b} + \frac{3L_b^{\,2}}{2N_A a^2} + \ln(\phi^m/e)\right) \tag{11}$$

where V is the volume of the system and ϕ^m is the A monomer concentration in the bulk after copolymer adsorption given by

$$\phi^m = \phi - \frac{S}{\pi R^2}\frac{pN_A}{V} \tag{12}$$

where ϕ is the total number concentration of A monomer in the system. The first term in eq 11 is the interfacial energy between the B block and water in the bulk solution; here A' is the B block surface area which can be determined by setting p equal to 1 in eq 4. The second term is the electrostatic energy of the chains, where L_b is the end-to-end distance of chains in the solution. The third term is the elastic contribution of the chains. The last one is the translational entropic contribution of the free chains. The excluded-volume term is not necessary to be included here because the chain extension is dominated by the monomer electrostatic repulsion and the copolymer solution concentration is dilute.

When the number of chains on the surface keeps increasing, the micelles or single chains begin to contact each other, and $L_s = R$. The charge of the adsorbed A block layer can be treated as a smeared-out distribution as long as the spacing of the A blocks is much less than the screening length.[37] For the condition of $L_s = R > N_A^{1/2}a$, the total free energy of the system is still given by eq 1. However, eqs 6 and 7 need to be modified to

$$F_s^{mc} = \frac{S}{\pi R^2}p\left(\frac{3R^2}{2N_A a^2} + \frac{\pi^2}{6}\frac{N_A a^2}{D^2}\right) \tag{13}$$

$$F_s^{mex} = \frac{\upsilon}{2}\left(\frac{pN_A}{\pi R^2 D}\right)^2 SD \tag{14}$$

The intramicelle or single chain electrostatic repulsion (eq 5) and the electrostatic repulsion energy between micelles or single chains on the surface (eq 9) are combined into the following equation:[37]

$$F_s^{er} = S\left(\frac{pN_A f}{\pi R^2}\right)^2\frac{\pi l_B}{D^2\kappa^3}(\exp(-2D\kappa) - 1 + 2D\kappa) \tag{15}$$

which is the electrostatic repulsion energy of the adsorbed copolymer layer. The total free energy is minimized to equate the chemical potentials of the free chains in the bulk solution with the chains on the surface. When the number of chains on the surface is low, the chains might exist as single chains. With the increase of the copolymer surface coverage, adsorbed chains aggregate together to decrease the interfacial energy of the B−water interface. In contrast to the micellization in a bulk solution, the micellization on a charged surface is a sharp transition. In a bulk solution, when the chain concentration is higher than the cmc, some chains form micelles to decrease the free energy, keeping the chain chemical potential constant at μ_{cmc}. In the presence of a charged surface, the correlation between adsorbed chains, either single or in micelles, induces the formation of a periodic structure, and the mixing entropy only has little contribution to the free energy. When the chemical potential of the chains in the bulk, μ, is equal to or larger than the chain chemical potential at the critical surface micellization concentration (csmc), μ_{csmc}, all of the chains on the surface form micelles because the formation of micelles does not decrease the chemical potential of the chains in the infinite bulk solution. Therefore, the micellization process does not stop until nearly all the chains on the surface form micelles.

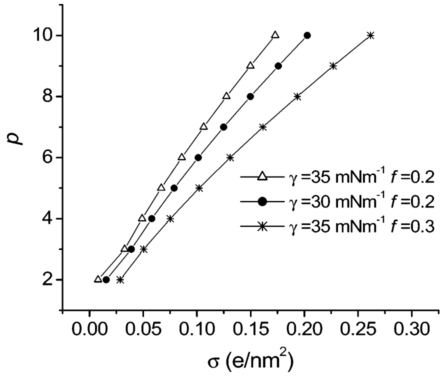

Figure 2. Aggregation number as a function of surface charge density. The following parameters are used in the calculation: $N_A = 150$, $N_B = 50$, $a = b = 0.5$ nm, and $v = a^3$. The salt concentration is 0.01 mM, and the monomer A concentration is 10^{-8} M. The values of surface tension of hydrophobic block and water interface γ and the fraction of charged monomers f are shown in the figure.

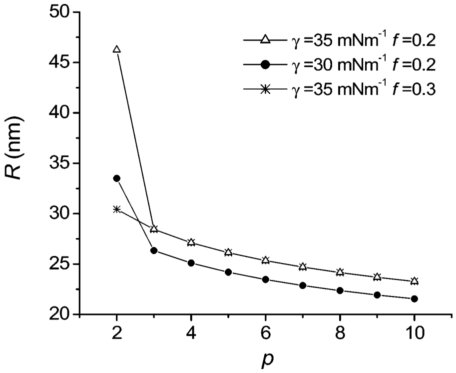

Figure 3. Variation of the micelle Wigner-Seitz cell size R as a function of the aggregation number p. The parameters used are the same as in Figure 2.

B. Results and Discussion. The surface tension of the B block−water interface in this paper is in the range of 30−40 mN m^{-1}, which is the typical value for the surface tension of hydrophobic organic materials−water.

In Figures 2 and 3, we show that with the increase of surface charge density the aggregation number, p, rises and the corresponding size of the cell declines. Those are general properties of copolymers. Equation 9 is used for the calculation of dilute surface adsorption regime. When copolymers have the same fraction of charged monomers, f in the A block, the copolymer with a higher surface tension of B−water interface, γ, can aggregate on a surface of lower charge density (△ and ● lines in Figure 2); the size of its Wigner-Seitz cell R is larger, that is, the amount of adsorbed chains on the surface is less (△ and ● lines in Figure 3). The copolymer adsorption amount increases with the surface charge density. To form micelles, the copolymer of lower γ needs a surface with higher surface charge density to reach higher surface concentration. Note that although the translational entropy of adsorbed chains is negligible, the surface induced copolymer micellization is still related to the surface chain concentration. This paradox can be understood as follows. Two separated charged copolymers have to overcome their electrostatic repulsion energy before they can aggregate. The smaller the distance is, the less the compensation of electrostatic energy required. The interfacial energy decrease upon micellization compensates the electrostatic energy. Therefore, copolymers of low surface tension need a high surface concentration to lead to aggregation. For the contact condition, the interfacial energy decrease still needs to compensate the chain elastic stretching resulting from the electrostatic repulsion. The elastic energy is less if there are more chains adsorbed onto the surface because the cell size or the chain lengths are shorter.

For copolymers with equal surface tension of B−water interface, the copolymer with larger f requires a higher surface charge density to aggregate; this can be seen by comparing lines △ and ∗ in Figure 2. Furthermore, the size of the Wigner-Seitz cell R of the copolymer with larger f is smaller in the dilute surface adsorption regime. At the contact condition, however, the two kinds of copolymers have the same cell size when the micelles have the same aggregation number as can be seen by comparing lines △ and ∗ in Figure 3. It is difficult to aggregate chains of large charge in the dilute surface adsorption regime due to the electrostatic repulsion. When the copolymers are in contact, the interfacial energy decrease upon aggregation only needs to balance the extension of the chains. At the same surface tension of the B−water interface and aggregation number, the interfacial energy reductions from micellization are identical for micelles formed by copolymers with different line charge densities. Consequently, it is not difficult to understand why the sizes of the cells are the same for different copolymer micelles. We must emphasize that a higher surface charge density is needed for copolymers with larger f value to reach the same micelle size. In dilute copolymer solutions, micelles with large aggregation numbers may be formed if the micelles can trap enough counterions to screen interactions between charged monomers. However, it is not easy to form large micelles on an oppositely charged surface in the dilute surface adsorption regime because the surface repels the counterions of the charged block. Hence, charged surface induced copolymer micellization should mostly occur at the contact condition.

At the contact condition, the effective charge of the surface ($pN_A f/\pi R^2 - \sigma$) is nearly neutral. Surface charge inversion appears in the dilute surface adsorption regime, as shown in Figure 3 where we get 8.0% charge inversion for $\gamma = 35$ mN m^{-1}, $f = 0.3$, $p = 2$; 8.8% charge inversion for $\gamma = 30$ mN m^{-1}, $f = 0.2$, $p = 2$; and 11.5% charge inversion for $\gamma = 35$ mN m^{-1}, $f = 0.2$, $p = 2$. The charge inversion is not strong in these cases because the salt concentration is low and the L_s (around 25 nm for three cases) is close to R. If eq 10 is used to calculate the lateral repulsion between micelles, the values of charge inversion are 26.9%, 26.1%, and 32.2%, respectively. Equation 10 assumes the micelle charges are in the center of their Wigner cells. This approximation exaggerates the salt screening effect when L_s is close to R, which makes the calculations show more copolymer adsorption and easier formation of micelles on surfaces. Equation 10 is a better approximation than eq 9 if L_s is much smaller than R, which is expected for copolymers with long hydrophobic blocks.

As expected, the excluded volume does not have apparent effects on the micellization since the electrostatic repulsion dominates. At high salt concentrations, the excluded-volume effect is more important than the Coulomb interactions when v is much larger than $f^2 D l_B/\kappa$. The effects of excluded volume for good solvents and short-range repulsions between monomers for Θ solvents on the polyelectrolyte layer thickness or conformation have been well studied.[51,52] Our calculated layer thickness is around 3 nm and decreases with surface charge density.

For the contact and low salt concentration conditions, we can obtain simple scaling results

$$\frac{R^2}{N_A a^2} - p^{-1/3}\gamma b^2 {N_B}^{2/3} \approx 0 \qquad (16)$$

Equation 16 is obtained by minimizing the free energy. There is a possibility of surface charge inversion when the lateral distance between adsorbed macroions or micelles is comparable to or larger than the screening length.[36,53,54] However, the charge density of the copolymer layer is nearly equal to the surface charge density at the contact condition, $R^2\sigma \approx pN_Af$ because, for our cases, the salt concentration is low and the screening length is much larger than the distance between neighboring chains. We get

$$R \approx N_A^{1/2} N_B^{1/4} (\gamma ab)^{3/8} (f/\sigma ab)^{1/8} (ab)^{1/2} \tag{17}$$

$$p \approx N_B^{1/2} (\gamma ab)^{3/4} (f/\sigma ab)^{-3/4} \tag{18}$$

The dependences on N_A and N_B of both R and p agree with theoretical results for neutral copolymer surface micellization in air in the limit of homogeneous surface coverage where $R^2 \approx pN_Aa^2$.[55] In our model this limit occurs when the homogeneous layer charge neutralizes the surface, at the contact condition where $R^2\sigma \approx pN_Af$. Our scaling agrees with the neutral case because at the contact condition the micelles hardly feel charges on the surface outside its own cell when the effective surface-layer charge density is close to neutral. The electrostatic effect is a function of the ratio $f/\sigma ab$. The dependence of R on f is weak because aggregation number tends to be less for larger f.

We find that the interfacial energy reduction from micellization balances the extension of chains, which is R^2/N_Aa^2. Since R^2/N_Aa^2 does not depend on N_A due to the condition $R^2\sigma \approx pN_Af$, one interested property obtained in eq 18 is that p is not affected by the degree of polymerization of the A block, N_A.

It is well-known that addition of salt to the bulk solution reduces the cmc because the electrostatic repulsion between the corona chains is weakened by the salt ion screening. However, for the charged surface induced micellization, the salt effect varies for different conditions. Here we use the same definition for the csmc as Ligoure.[24] That is, the micellization point on the surface is $p = 2$, and the csmc is the corresponding bulk copolymer concentration. A feature of charged surface induced micellization is that the structure of the chains (R and L_s for the dilute surface adsorption regime and R for contact condition) on a charged surface at the csmc is only determined by the characteristics of the copolymer, but it is not determined by the surface charge density. This conclusion can be reached from eq 16 for the contact condition and is also correct for the dilute surface adsorption regime. This is because the electrostatic attractions between chains and oppositely charged surfaces are the same whether the chains are aggregated or single, as long as $D\kappa$ is much less than 1, and no chain is dangled in solutions with one end grafted in the micelle core. Copolymers form associated states when the copolymer surface concentration is higher than a certain value, which scales as $\gamma^{-1}N_A^{-1}N_B^{-2/3}a^{-2}b^{-2}$ for the contact condition. The surface charge density has to be high enough to make the surface copolymer concentration reach this value. The minimum surface charge density for surface induced micellization scales as $f\gamma^{-1}N_B^{-2/3}a^{-2}b^{-2}$ at the contact condition. The variation of the cscm with salt concentration at the condition $D\kappa < 1$ can be explained by a simple equation, eq 19, which is also obtained by minimizing the free energy

$$\ln \phi_{\mathrm{scmc}} = \alpha N_A f \frac{l_B}{\kappa}\left(\frac{pN_Af}{\pi R^2} - \sigma\right) - \beta \tag{19}$$

In eq 19 α and β are positive and do not include κ. The term $N_Af(l_B/\kappa)(pN_Af/\pi R^2)$ is the correlation between one chain and other adsorbed chains; the term $N_Afl_B\sigma/\kappa$ is the ion screened attraction of one chain with the surface and is the driving term for copolymer micellization on the surface at the bulk copolymer concentration less than the cmc. When the surface charge density σ is larger than the layer charge density, $pN_Af/\pi R^2$, the attraction term is predominant. Addition of salt increases the value of the right side in eq 19, that is, weakens the attraction, and then the csmc is higher. If the correlation term dominates, the csmc decreases with the addition of salt concentration. In our calculation, we assume that the short-range interaction between the charged surface and water is identical to that of the A blocks and the water and do not consider the net short-range interaction between the A blocks and the surface. In a real situation, short-range interactions between the surface and the A blocks are also involved. If there is a net short-range attraction between charged blocks and a surface besides the electrostatic attraction, the surface can be easily overcharged and the correlation term prevails. Addition of salt reduces the csmc. The opposite result occurs when there is a net short-range repulsion.

There are two major assumptions in our calculation. One is the monodispersity of charged micelles on the surface. To prove the first assumption, we consider the coexistence of single chains and micelles with certain aggregation number on the surface. The total free energy obtained through modifying the model in section II.A is $F = yF_s^c + (1 - y)F_s^m + F_s^{ea} + F_s^{er} + F_b^c$, where y is the fraction of surface area conquered by single chains and $1 - y$ the fraction of surface area conquered by micelles. We assume every chain or micelle stay in their Wigner cells. The Wigner cell size of micelles is p times of that of single chains due to the correlation hole effect. We then add the translational entropy of the chains by assuming the single chains or micelles have the possibility to be anywhere in their cells. This is an overestimation of the entropy, which could lead to the coexistence of aggregated and of free chains on the surface. In reality, the charged chains or micelles prefer to stay in the center of their cell due to lateral correlations. Our results show that there is no coexistence: chains on the surface are either all free or all aggregated into micelles. This is because the translational entropy can be extremely large for uncharged chains in bulk solutions, but it is small for charged chains on an oppositely charged surface because of the correlation hole effect.

The second assumption is that surface micelle chains are relatively flat and do not dangle in solutions with one end grafted in the micelle core. This is valid for our considered low salt concentration regime. Chains dangling in solutions with one end grafted in the micelle core experience less electrostatic repulsion from the other chains and less attraction from the charged surface. When L_s is equal to R, the surface charge is nearly neutralized by adsorbed chains at low salt concentration. If there are some dangling chains, the absolute value of the surface charge must be larger than the adsorbed relatively flat chains. Therefore, a net electrostatic attraction between the surface and the dangling chains occurs. Consequently, chains become flat in the lowest energy state. On the other hand, when R is much larger than L_s, dangling reduces the electrostatic repulsion and hardly decreases the electrostatic attraction. In this regime indeed dangling ends is the favorite conformation, as shown in the Appendix. It is very difficult however to induce micelle formation when R is much larger than L_s. Our calculated results show that R is slightly larger than L_s. Only when micelles are already formed in the bulk solution, they may have a cap conformation rather than a relative flat conformation on the surface when R is much larger than L_s.

III. System with Weak Charge Groups

Most charge groups are partially ionized or associated with hydrogen ions at a wide range of pH values. In this case, the approach described in section II for fixed charges has to be modified to include the effect of the reactions that generate the charge groups. The reactions can be written as

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$$

$$\mathrm{C} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{CH^+} + \mathrm{H_2O}$$

Here we consider that HA are monomers in the A blocks and become negatively charged through the release of hydrogen ions. The surface is positively charged through the association between the surface groups, C, and the hydrogen ions. One experimentally used system is amino group terminated surfaces and poly(methacrylic acid/ethyl acrylate) as charged blocks in the copolymers.

A. Model of Surface Micellization. For simplicity, we only provide the model of systems with weak charge groups at the contact condition which is the condition necessary to easily form micelles. In the case of systems with weak charged groups, one needs to include the energy changes due to the reactions of the association and ionization in the free energy (eq 1)

$$F_s^b = -S\rho f_b \ln K_b \tag{20}$$

$$F_s^a = -\frac{S}{\pi R^2} pN_A f_{sa} f \ln K_a \tag{21}$$

$$F_b^a/V = -\phi^m f_{ba} f \ln K_a \tag{22}$$

Here, F_s^b is the energy resulting from the association of surface groups and hydrogen ions, K_b is the association constant, ρ is the surface group density on a surface, and f_b is the fraction of reacted surface groups. Then $S\rho f_b$ is the total number of reacted surface groups. In eqs 21 and 22, F_s^a and F_b^a are the dissociation energy from the ionized monomers on the surface and in the bulk, respectively. K_a is the dissociation constant, and f is the fraction of ionizable monomers in the charged block. Because of the effect of the electrostatic potential, copolymers on the surface and in the bulk have different fractions of ionized monomers, which are f_{sa} and f_{ba}, respectively.

The entropic contribution of the reactions to free energy due to mixing the charged and uncharged groups is given by

$$F_s^{en} = S\rho[f_b \ln f_b + (1 - f_b)\ln(1 - f_b)] + \frac{S}{\pi R^2} pN_A f[f_{sa} \ln f_{sa} + (1 - f_{sa})\ln(1 - f_{sa})] \tag{23}$$

$$F_b^{en}/V = \phi^m f[f_{ba} \ln f_{ba} + (1 - f_{ba})\ln(1 - f_{ba})] \tag{24}$$

The electrostatic attraction energy between charged A blocks and the oppositely charged surface, F_s^{ea}, and the repulsion of the copolymer layer on the surface, F_s^{er}, have the same forms of eqs 8 and 15, respectively, but replace f by $f_{sa}f$ and σ by ρf_b.

The self-repulsion energy of charged surface groups can be written as

$$F_s^{es} = 2\pi S(\rho f_b)^2 \frac{l_B}{\kappa} \tag{25}$$

When $D\kappa$ is much less than 1, the summation of all the electrostatic contributions is

$$F_s^e = 2\pi S\left(\rho f_b - \frac{pN_A f_{sa} f}{\pi R^2}\right)^2 \frac{l_B}{\kappa} \tag{26}$$

The bulk free energy is given by

$$\frac{F_b^c}{V} = \frac{\phi^m}{N_A}\left(\gamma A' + \frac{l_B N_A^{\,2} f^2 f_{ba}^{\,2}}{L_b} + \frac{3L_b^{\,2}}{2N_A a^2} + \ln(\phi^m/e)\right) + \left(\frac{SpN_A f_{sa} f}{\pi R^2 V} - \frac{S\rho f_b}{V} + \phi^m f_{ba} f + c_{HCl}\right) \ln\left(\frac{SpN_A f_{sa} f}{\pi R^2 V} - \frac{S\rho f_b}{V} + \phi^m f_{ba} f + c_{HCl}\right)/e \tag{27}$$

The last term is the translational entropic contribution of hydrated hydrogen ions. In it, $(SpN_A f_{sa} f/\pi R^2 V) - (S\rho f_b/V)$ is the bulk hydrogen ion concentration variation because of the reaction on the surface, and c_{HCl} is the initial hydrogen ion concentration in the solution. The subscript of HCl is used because hydrochloride is commonly employed in experiments to adjust the hydrogen ion concentration. We use simple terms for the free energy of the dilute solution and ignore structural correlations, which have been included in the bulk semidilute polyelectrolyte titration studies.[56] The equilibrium state is obtained by minimizing the total free energy with respect to f_b, f_{ba}, f_{sa}, L_b, p, D, and $S/\pi R^2$. The model of the systems with weak charge groups in the dilute surface adsorption regime has similar modifications.

B. Results and Discussion. In this section we give results for a model system consisting of silicon substrates modified with 3-aminopropyltriethoxysilane, which are widely used as positive charged surfaces. The pK_b of the association between 3-aminopropyltriethoxysilane and hydrated hydrogen ion is −10.5. The charged block is composed by ethyl acrylate monomer and methacrylic acid monomer. Methacrylic acid monomer can ionize and has a fraction f in the charged block. Here we use the dissociation constant of 2-methylpropanoic acid (pK_a = 4.8) for methacrylic acid monomer. In ref 56, the pK_a of methacrylic acid, 4.5, is used directly. The backbone of the charged block is composed of single bonds, and there is a double bond in methacrylic acid. Since the electron distribution in a double bond is very different from that of a single bond, it is appropriate to use the pK_a of 2-methylpropanoic acid rather than that of methacrylic acid. The possible formation of ion pair $-\mathrm{COONH_3}-$ is not included in our model. Since we only described the model of the contact condition for the system of weak charge groups, we chose parameters in our calculation so that the copolymer surface coverage belongs to this regime.

Figure 4 gives the variation of the fraction of dissociated methacrylic acid monomer in the solution, f_{ba}, and on the surface, f_{sa}, with pH. Nearly all of the amino groups associate with hydrogen ions in the considered pH range. Calculation is consistent with the common knowledge that amino groups are strong charge groups when the solution pH is less than 7. Meanwhile, the amino groups are partially charged in base solutions. Both f_{ba} and f_{sa} rise as pH increases. Electrostatic repulsion energy between charged monomers inhibits further dissociation of methacrylic acid monomers. Since the monomers on the surface experience a smaller electrostatic repulsion than the monomers in the bulk do, f_{sa} is larger than f_{ba}.

The variation of aggregation number p and the size of micelle R with pH are illustrated in Figures 5 and 6. Although there

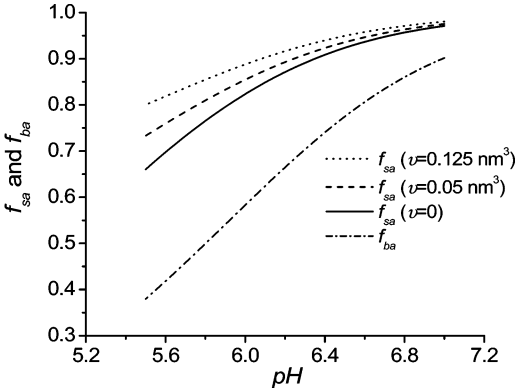

Figure 4. pH dependence of the fractions of ionized monomers on the surface f_{sa} and in the bulk f_{ba}. The following parameters are used: $N_A = 300$, $N_B = 20$, $\gamma = 35$ mN m^{-1}, $f = 0.5$, and $a = b = 0.5$ nm; surface amino group density $\rho = 1/\text{nm}^2$, salt concentration 0.01 mM, and monomer A concentration 10^{-8} M.

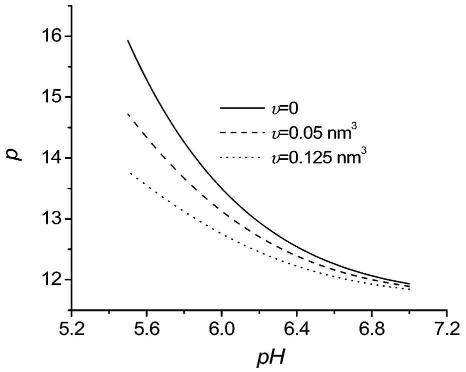

Figure 5. Variation of the aggregation number as a function of pH. The parameters used are the same as in Figure 4.

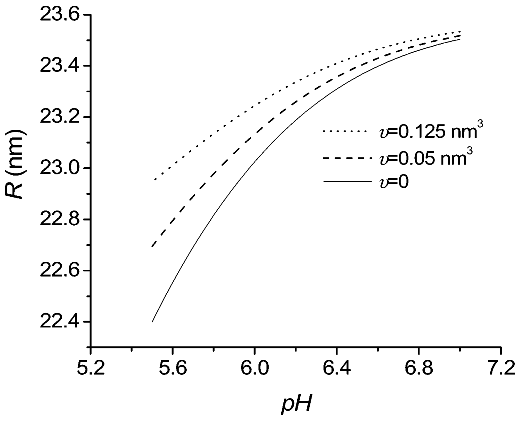

Figure 6. Increment of the micelle size with the rise of pH. The parameters used are the same as in Figure 4.

are many variables for a system with weak charge groups, eq 16 is still valid. The scaling results of R and p are similar to eqs 17 and 18

$$R \approx {N_A}^{1/2}{N_B}^{1/4}\gamma^{3/8}(\rho f_b)^{-1/8}(f_{sa}f)^{1/8}a^{3/4}b^{3/4} \tag{28}$$

$$p \approx {N_B}^{1/2}\gamma^{3/4}(\rho f_b)^{3/4}(f_{sa}f)^{-3/4}a^{3/2}b^{3/2} \tag{29}$$

Since f_b is close to one and f_{sa} increases with pH value, the aggregation number reduces with the pH value as the number of charged monomers in one chain becomes larger (Figure 5). Simultaneously, the micelle size expands (Figure 6). Although eqs 28 and 29 clearly tell us the tendency, R and p cannot be estimated directly from eqs 28 and 29 because f_{sa} can only be evaluated through a self-consistent calculation. The dependence of R and p on pH might change if f_b is sensitive to pH. When the surface groups are acid groups and the monomers are base groups, the pH effect should be reversed.

Interesting results shown in Figures 4−6 are the importance of excluded-volume effects which do not affect the system with strong charge groups when the salt concentration is low. One characteristic of systems with weak charge groups is that the charges are adjustable according to local environments. With the decrease of pH value, the amount of adsorbed chains has a tendency to rise due to the weaker ionization of monomers in the A block and results in the increase of excluded-volume repulsion energy. To prevent further increase, charged A blocks on the surface try to keep the ionization degree unchanged when the pH decreases so that less chains are needed to be adsorbed onto the surface to neutralize the surface charge. Therefore, the structure of micelles does not experience a huge change during pH variation if there is a large excluded-volume effect (Figures 5 and 6). We expect the excluded volume to have a more significant buffering effect when it is comparable to the electrostatic interaction at high salt concentration or when the A blocks can form hydrogen bonds with water molecules.

IV. Conclusion

We develop a two-state model to study charged surface induced diblock copolymer micellization resulting from the electrostatic attraction between a surface and charged blocks when the bulk concentration is less than cmc. Systems with strong charge groups and systems with weak charge groups are both considered.

For systems with strong charge groups, we investigate two conditions. One is the dilute surface adsorption regime at which the size of a single chain or micelle on the surface, L_s, is smaller than the size of their Wigner-Seitz cell R. The second is the contact condition, where $L_s = R > N_A^{1/2}a$. It is difficult to induce micellization in the dilute surface adsorption regime due to the repulsion among the charged blocks on the surface. At the contact condition, we obtain the scaling dependence of micelle size R and aggregation number p as a function of the blocks' polymerization degrees N_A and N_B, the hydrophobic block and water surface tension γ, fraction of charged monomers f, and the surface charge density σ. We find that R and p have the same dependence on N_A and N_B as an uncharged system. The electrostatic effect is reflected in the scaling $R \sim (f/\sigma)^{1/8}$ and $p \sim (f/\sigma)^{-3/4}$. To experimentally check the scaling predictions in our paper, one needs to precisely control the degree of polymerization of the two blocks and the fraction of ionizable monomers in the charged block by ionic polymerization or other methods. To detect the value of f_{sa} and f_b, Fourier transform infrared spectroscopy (FTIR) in the mode of attenuated total reflection (ATR) can be used.

As it is well-known, increasing salt concentration decreases the cmc in the bulk. However, for charged surface induced micellization, the salt effect varies at different conditions. When the electrostatic attraction between the surface and the charged blocks is larger than the correlation between the adsorbed chains, the addition of salt reduces the net attraction and increases the csmc. This is a general situation when there is a short-range repulsion between the charged block and the surface. On the other hand, as the electrostatic repulsion between adsorbed chains is predominant, the result is opposite.

For systems with weak charge groups we consider an amino group terminated surface and poly(methacrylic acid/ethyl acrylate) as the copolymer charged block. Nearly 100% of the surface groups are found to associate with hydrogen ions in the pH range of 5.5−7. We neglect here fluctuations because our chains have large fraction of charged monomers and the degree of adsorption is large. The fractions of ionized monomers in the bulk and on the surface, determined self-consistently here, rise with the pH. This partial ionization effect of adsorbed copolymer layers is very important to determine the possibility of subsequent adsorption of counterions or other oppositely charged macroions; for example, it might explain the layer-by-layer anionic and cationic polyelectrolyte self-assembly.[57−61] Formation of the polyelectrolyte multilayers has been attributed to the charge inversion.[62,63] However, unlike strongly charged polyelectrolytes, it is difficult for weakly charged polyelectrolytes to create a large surface charge inversion in a dilute salt solution. At this condition, the reason might be partial ionization. After adsorption, the surface is nearly neutral. When the substrate is dipped into an oppositely charged polyelectrolyte solution, the oppositely charged polyelectrolytes approach the surface and promote the ionization of the previous layer,[61] and a strong electrostatic attraction results. Scaling results similar to those for systems with strong charge groups are obtained. We also find that R increases and p decreases with pH value. These tendencies of R and p with pH might change when f_b is sensitive to pH variations.

The excluded-volume effect does not change the micelle size and aggregation number for systems with strong charge groups at low salt concentration, as expected. However, it has a significant buffering effect on the micelle size and aggregation number when the pH varies for systems with weak charge groups.

Most hydrophobic blocks in diblock copolymers have a high glass transition temperature, T_g, such as polystyrene. These copolymers are not able to reach equilibrium due to the stability of their glassy core. To test our theory, copolymers with low-T_g hydrophobic block should be used. For example, Förster et al.[64,65] reported micelles formed by poly(ethylethylene-*b*-styrenesulfonic acid) (PEE−PSSH), in which the hydrophobic block PEE has $T_g = -25$ °C; the results of these equilibrium bulk micelles are well explained by theoretical predictions of bulk micellization.[13] Atomic force microscopy (AFM) can be employed to study charged surface induced micellization. However, AFM only can detect the size and shape of the micelle core and the distance between micelles. The radius of the micelle cannot be detected directly.[66]

In this paper, we show the adsorbed chains are relatively flat on the surface, and there are no chains dangling on the surface with grafted blocks in the micelle core when the distance between micelles is around the Wigner cell size. In the opposite limit when the distance between micelles is very large, it is possible to have dangling chains, but in this regime it is easy to form micelles in the bulk. In all the regimes, the micelle aggregation number increases with the surface charge density. Wormlike micelles are expected to appear when the aggregation number is very large. The transition of the micelle conformation is a subject of future study.

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Appendix. Charged Surface Induced Semispherical Micelles

In the paper, we have discussed relatively flat micelles. This is reasonable in the semidilute surface adsorption regime (contact condition) at low salt concentrations. However, it is still possible for copolymers to form semicap or semispherical micelles on the surface in the dilute surface adsorption regime (separate condition). The transition between these two kinds of micelles is when one chain is dangling on the surface with the hydrophobic block grafted in the micelle core. This dangling chain conformation is energetically favorable when the chain experiences a net electrostatic repulsion from the surface-relatively flat copolymer layer. To find the transition point, we need to compare the electrostatic repulsion and attraction to the dangling chain from other micelle chains and surface charge in their Wigner cell. The energy terms are calculated by simply assuming the center of charges is located at the distance h from the charged substrate. We also assume the screening length at the surface is the same as in the bulk. The electrostatic attraction from the surface charge in the Wigner cell is given by

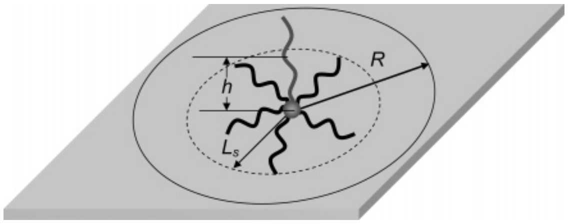

Figure 7. Sketch of a semispherical diblock copolymer micelle on a charged surface in the dilute regime or separated condition.

$$F_{\mathrm{att}} \approx -2\pi l_B f N\sigma \int_0^R \frac{\exp(-\kappa\sqrt{r^2+h^2})}{\sqrt{r^2+h^2}}\, r\, \mathrm{d}r = 2\pi \frac{l_B}{\kappa} f N\sigma \exp(-\kappa h)(\exp(\kappa h - \kappa\sqrt{R^2+h^2}) - 1) \quad \text{(A1)}$$

The electrostatic repulsion from other micelle chains can be written in a similar form

$$F_{\mathrm{rep}} \approx -2\pi \frac{l_B}{\kappa} f N \frac{(p-1)f N}{\pi R^2} \exp(-\kappa h)(\exp(\kappa h - \kappa\sqrt{L_s^{\,2}+h^2}) - 1) \quad \text{(A2)}$$

At low salt concentrations, κh is much smaller than one. Moreover, since R and L_s are larger than h, we can linearize the exponential terms and get the condition when the repulsion is larger than the attraction

$$\frac{(p-1)f N}{\pi R^2 \sigma} \frac{R}{L_s} > 1 \quad \text{(A3)}$$

When the aggregation number p is large, $(p-1)fN/\pi R^2\sigma$ is roughly the charge ratio of the micelles and the surface. It has being shown that starlike polyelectrolyte adsorption on charged surfaces could generate large surface charge inversion and that the distance between neighboring starlike polyelectrolytes can be much larger than the size of the polyelectrolytes.[54] It seems that the surface induced micelles could also be semispherical if the aggregation number and the distance between micelles are both large. However, we have shown in this paper that the aggregation number is very small for the dilute surface adsorption regime unless the copolymers have long hydrophobic blocks with large surface tension. At this condition the copolymers have very low bulk cmc. Therefore, a semispherical structure is possible but rare for the case of charged surface induced micellization.

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