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Self-Assembly of Block Copolymers with a Strongly Charged and a Hydrophobic Block in a Selective, Polar Solvent. Micelles and Adsorbed Layers

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ABSTRACT: The aggregation of diblock copolymers consisting of a neutral block (A) and a polyelectrolyte block (P) in aqueous salt solution, a precipitant for the A block, is examined using a scaling model. Two self-assembled structures are discussed: micelles and adsorbed layers, as well as the equilibrium between them. The salt concentrations considered are moderately high, so that the electrostatic persistence length of the charged block is smaller than the range of excluded volume correlations. The aggregation number of micelles and the surface density adsorbed layers were found to increase, and the charged block thickness to decrease, with salt concentration. Micellar phase properties are predicted to be similar to those of neutral copolymers in nonpolar solvents. Layers adsorbed from dilute copolymer solutions, below the critical micelle concentration, obtain a higher surface density than layers at equilibrium with micellar solutions. The thickness of the charged block was found to be similar, in the latter case, to that of the micelle corona.

I. Introduction

The amphiphilic nature of diblock copolymers is manifested, in the presence of a selective medium, in self-assembly phenomena.[1,2] Selective solvation, due to either a selective solvent or a selective surface, gives rise to formation of aggregates such as micelles, microemulsions, and adsorbed polymer layers. This characteristic of diblock copolymers has led to their use as surface modifying agents in colloidal suspensions and at other polymer interfaces. As such, they are required to prevent spontaneous coagulation of particle, while not hindering eventual compression into ordered, dense structures. The modified interparticle potential can be also used to adjust suspension rheological and mechanical properties during processing. Better understanding of the nature and character of the adsorbed diblock copolymer layers, and how they are related to copolymer structure and properties, is therefore necessary.

The equilibrium properties of neutral diblock copolymer adsorbed layers, and micelles, in a selective solvent, were discussed by Marques et al.[1] The selective solvent is a precipitant for one block, causing that block to aggregate and form a molten core droplet, or an adsorbed dense film on a surface. The well-solvated block forms a corona, or brush, densely tethered through the precipitated core block (see Figure 1). Aggregate characteristics are controlled, under ideal circumstances, by thermodynamic equilibrium: a balance between interfacial tension and chain stretching energies. In the case of adsorbed layers, the interactions between the core, or anchor, block and the surface also play an important role. The structure of an adsorbed copolymer layer was analyzed[1] considering the equilibrium between the layer and a reservoir solution with a chemical potential μ_{ex}. The adsorbed layer was divided into two regions: one, of the insoluble core block, forming a molten film adjacent to the surface, and the other of the solvated block brush. Micelle structure was assumed to consist of two spherically symmetrical regions, equivalent to the adsorbed layer regions. The aggregation number, critical micelle concentration, and chemical potential of the copolymer micelles were calculated. Finally, the effect of micellization in the bulk solution on the reservoir potential, and hence on the adsorbed layer structure, was estimated via minimization of the grand canonical free energy.[1]

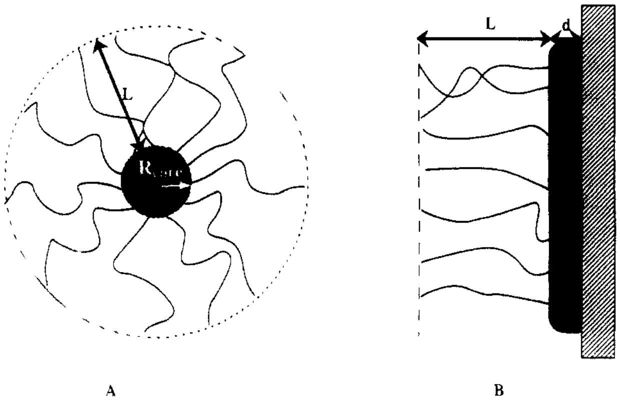

Figure 1. Diblock copolymer aggregates: (A, micelles). The neutral block forms a dense core of radius R_{core}. The copolymer junction points are restricted to the core-corona interface, grafting the charged block. L is the thickness of the charged block corona. (B, adsorbed layers): The neutral block adsorbed on the surface, aggregating into a film of thickness d. The charged block, grafted through the neutral block, forms a brush of thickness L.

Various colloidal systems (for example, latex paints) are suspended, not in nonpolar solvents but in aqueous solutions. Water-soluble chains, such as charged polymers, are needed to stabilize such suspensions. The properties of charged polymers in polar solvents differ from those of neutral polymers in a good solvent, due to the effect of electrostatic interactions. Under extreme conditions, corresponding to dilute salt concentration and high charge density along the backbone, electrostatic correlations dominate chain configurations, and, therefore, aggregation characteristics. For example, it has recently been predicted theoretically[3] that micellization of charged-neutral diblock copolymers (our term for diblock copolymers with a highly charged polyelectrolyte block and a hydrophobic block), in dilute salt solutions, will not take place unless the charged block is short compared to the core block. This differs from neutral copolymer micellization in nonpolar solvents, where "starlike" micelles are obtainable.[4] As the solution salt concentration increases, screening effects reduce the range of electrostatic interactions, and the chain

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regains some flexibility. In very high salt concentrations, electrostatic interactions are, in effect, completely screened and the charged chain conformation is indistinguishable from that of a neutral one. In this study, we calculate the equilibrium properties of charged-neutral diblock copolymer aggregates in aqueous salt solutions of moderate concentration, between the two extremes. In such solutions, the range of excluded volume interactions is higher than that of the electrostatic correlation length, so that the charged block configurations depend on both.

The paper is organized as follows. In the next section, we apply a scaling "blob" model to highly charged chains in aqueous salt solution, in both planar and spherical geometries. We employ this model in section III in the analysis of charged-neutral micelle phase and in section IV to adsorbed layers in equilibrium with either dilute copolymer solutions or a micellar phase.

II. Scaling Model of Grafted, Highly Charged Chains in Aqueous Salt Solutions: Brushes and Stars

We modify a scaling model of dense polymer brushes[5,6] and apply it to charged chains in aqueous salt solutions.[7,8] In this approach, which allows for excluded volume interactions, a semidilute solution of neutral polymer chains is envisioned as a succession of units or "blobs" of a correlation length ξ. The blob size is independent of chain molecular weight, a function of the local segment concentration only. Inside the blob, excluded volume interactions dominate, implying that a chain segment obeys self-avoiding walk statistics:

$$\xi \sim a g^{3/5} \tag{1}$$

where g is the number of segments in a blob and a is a segment size. (We use the symbol "$\sim$" in this paper to mean equal within a numerical factor of order 1.) The local dimensionless segment concentration ϕ, which is proportional to the number of segments per unit volume, can be related to ξ via the relationship

$$\phi \sim g(a/\xi)^3 \sim (a/\xi)^{4/3} \tag{2}$$

Outside the blob all excluded volume interactions are screened and the chain of blobs is Gaussian. In the case of densely grafted chains, or a polymer brush, where the distance between graft points is much smaller than the free chain radius of gyration, the chain of blobs is stretched (see Figure 2). The chain length L is therefore proportional to ξ times the number of blobs N/g, where N is the number of segments per chain

$$L \sim \xi(N/g) \sim aN\phi^{1/2} \tag{3}$$

In planar geometry, the local concentration is assumed to be the same as the global segment concentration. Therefore, $\phi \sim N\sigma a/L$, where σ is the dimensionless surface density (a^2/ξ^2). The brush thickness scales as

$$L \sim aN\sigma^{1/3} \tag{4}$$

Each blob comprises a free energy of order kT, where k is the Boltzmann's constant and T the temperature.[6] The kT per blob ansatz can be explained by considering chain stretching. The free chain of blobs is Gaussian, while the grafted chain is stretched: The elastic energy of the chain, relative to kT, scales as $\{L/R_g\}^2 \sim \{\xi(N/g)/\xi(N/g)^{1/2}\}^2 \sim (N/g)$ namely, equal to the number of blobs per chain

$$F/kT \sim \frac{N}{g} \sim N\phi^{5/4} \sim N\sigma^{5/6} \tag{5}$$

In aqueous solutions, two long range interactions affect the charged chain conformations: excluded volume and electrostatic. As in the neutral brush, ξ defines the range of excluded volume interactions, while the range of electrostatic interactions is described by an electrostatic persistence length, b. We are interested in the case where b is smaller than the excluded volume correlation length (but larger than a), so that over length scales larger than b but smaller than ξ chain segments follow self-avoiding walk statistics. Over distances smaller than b, electrostatic forces stiffen the chain.[7,10,11] Assuming that each segment carries a monovalent charge (highly charged limit), we can envision the blob as composed of g rodlike segments, each containing b/a segments. The persistence length, b, is inversely proportional to the square of the Debye length κ.[10,11] For monovalent electrolytes, κ^2 scales as the salt concentration ϕ_s, so that b decreases with increasing salt concentration. This limits our discussion to systems where $\phi_s > \phi^{3/4}$. Equations 1 and 2 are valid in this regime if the segment size, a, is substituted by the electrostatic persistence length b. We find that the excluded volume correlation length scales as

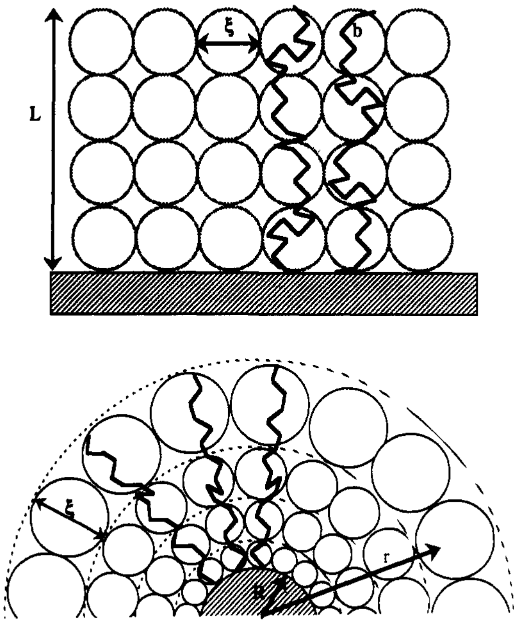

Figure 2. Blob model for charged chains. Three size scales can be distinguished: The electric persistence length b, the blob size or excluded volume interaction range ξ, and the brush thickness L.

$$\xi \sim b g^{3/5} \sim a \frac{\phi_s^{1/2}}{\phi^{3/4}} \tag{6}$$

as calculated by Joanny and Pincus.[7] The kT per blob ansatz still holds, as in the neutral chain brush, since electrostatic repulsion is accounted for via the electrostatic persistence length. The number of segments in a blob is gb/a, so that the number of blobs is equal to $aN/(bg)$. In the planar geometry where $\phi \sim N\sigma a/L$

$$L \sim N \frac{\sigma^{1/3}}{\phi_s^{2/3}} \tag{7}$$

$$F/kT \sim N \frac{\sigma^{5/6}}{\phi_s^{2/3}} \tag{8}$$

The charged chain free energy is higher than that of the neutral chain (eq 2) due to the electrostatic interactions. As expected, both brush thickness and free energy decrease as the effective screening of electrostatics, namely, the salt concentration, increases. The brush thickness described in eq 7 is similar to that calculated by Pincus[12] and by Argillier and Tirrell[9] using a mean field approach. As is usual when comparing mean field and scaling calculations, the chain free energy of eq 8 is lower than the mean field result by $\sigma^{1/6}/\phi_s^{1/3}$. The condition that ϕ_s be larger than $\phi^{3/4}$ is reduced to $\phi_s > \sigma$.

This analysis can be extended to chains grafted on a spherically curved surface of radius R (see Figure 2). The blob scheme remains the same, but the increase in volume as a function of the radius r is incorporated via a monotonically increasing correlation length ξ. Combining the Daoud–Cotton model[13] for a star with f arms, where $\xi \sim r/f^{1/2}$ with eq 6, we find a relationship between the local segment concentration, the radius, and the salt concentration:

$$\phi(r) \sim f^{2/3}\phi_s^{2/3}(a/r)^{4/3} \tag{9}$$

The brush thickness is determined by the stipulation that the segment concentration account for all segments in the system

$$fNa^3 \sim \int r^2\, \phi(r)\, \mathrm{d}r \tag{10}$$

$$L/R \sim \{1 + Nf^{1/3}(a/R)^{5/3}/\phi_s^{2/3}\}^{3/5} - 1 \tag{11}$$

In the limit of small interface radii and high chain molecular weight (starlike configuration), equation 11 is reduced to

$$L \sim aN^{3/5}\frac{f^{1/5}}{\phi_s^{2/5}} \tag{12}$$

The free energy (per chain), proportional to the number of blobs, scales as

$$F/kT \sim \int r^2\, \mathrm{d}r/\xi^3 \sim f^{1/2}\ln(1 + L/R) \sim f^{1/2}\ln(1 + Nf^{1/3}(a/R)^{5/3}/\phi_s^{2/3}) \tag{13}$$

As in the planar brush, both the brush thickness and chain free energy decrease with increasing salt concentration. However, the effect of salt concentration is much smaller in the spherical brush. The expression for the free energy of a highly charged chain in aqueous salt solution grafted on a spherical surface is identical, within a logarithmic factor, to that of a neutral polymer chain in a nonpolar solvent,[2] unlike the planar charged brush which has a much higher free energy than the planar neutral brush. Thus, charged brushes gain more free energy with interface curvature, compared to their neutral counterparts.

III. Micellar Phase Formation

A. Single Particle Properties. Diblock copolymers in a selective solvent form aggregates, or micelles, when the copolymer concentration exceeds a critical value. Such is the case of neutral-charged copolymers in aqueous solution. The micelles consist of two concentric regions: an inner core of the insoluble neutral A block, and an outer corona of swollen charged P block (see Figure 1). The aggregation number, f, is the key variable which determines all aggregate properties, namely, the surface density and micelle radius. We study these micelles following the simplified model proposed by Halperin,[4] and Marques et al.,[1] for neutral copolymer micelles. The micelles are assumed to be monodisperse, and their concentration low so as to exclude micelle–micelle interactions. We also assume that the blocks are extremely incompatible and the solvent is highly selective, so that the core–corona interface, to which the copolymer junction points are constrained, is sharp. The high solvent selectivity precludes any significant swelling of the core, and the A core is be treated as a molten droplet. The core volume is therefore equal to the volume of A segments in a micelle, and R_{core}, the core radius, scales as

$$R_{\text{core}} \sim a(N_A f)^{1/3} \tag{14}$$

where N_A is the number of segments in A block. The free energy of a single micelle consists of three contributions, associated with the core–corona interface and each of the copolymer blocks. The interfacial energy is proportional to the interface area of the micelle ($\sim R_{\text{core}}^2$) times the interfacial tension (γ). The stretching penalty due to aggregation of the core block, which is the melt state, scales as

$$F_A/kT \sim \frac{R_{\text{core}}^{\ 2}}{a^2N_A} \sim f^{2/3}/N_A^{1/3} \tag{15}$$

The charged block is effectively grafted to a spherical surface of radius R_{core}, so that the model of grafted chains described in section II applies. Limiting our discussion to asymmetric copolymers ($N_A < N_P$, where N_P is the number of segments in the charged block), the thickness of the swollen corona, L, is therefore much larger than the collapsed core radius, R, or, $L/R \gg 1$. The micelle is "starlike",[4] and the free energy of the P block (eq 13) can be approximated by

$$F_p/kT \sim f^{1/2}\ln(L/R) \sim f^{1/2}\ln\left\{\frac{N_P f^{1/3}(a/R)^{5/3}}{\phi_s^{2/3}}\right\} \tag{16}$$

Combining the three contributions, we can write the free energy (per chain) of the micelle

$$F_m/fkT \sim (\gamma a^2/kT)N_A^{2/3}/f^{1/3} + f^{2/3}/N_A^{1/3} + f^{1/2}\ln\left\{\frac{N_P}{N_A^{5/9}f^{2/9}\phi_s^{2/3}}\right\} \tag{17}$$

The micelle properties are obtained by minimization of the free energy with respect to f:

$$-(\gamma a^2/kT)N_A^{2/3}/f^{4/3} + f^{-1/3}/N_A^{1/3} + f^{-1/2}\ln\left\{\frac{N_P}{N_A^{5/9}f^{2/9}\phi_s^{2/3}}\right\} - f^{1/2}(1/f) = 0 \tag{18}$$

Neglecting the A block stretching (second term) and assuming the logarithmic term is approximately constant

$$f \sim \frac{(\gamma a^2/kT)^{6/5}N_A^{4/5}}{\{\ln(N_P/N_A^{5/9}f^{2/9}\phi_s^{2/3})\}^{6/5}} \sim (\gamma a^2/kT)^{6/5}N_A^{4/5} \tag{19}$$

and

$$R_{\text{core}} \sim a\frac{(\gamma a^2/kT)^{2/5}N_A^{3/5}}{\{\ln(N_P/N_A^{5/9}f^{2/9}\phi_s^{2/3})\}^{2/5}} \sim (\gamma a^2/kT)^{2/5}N_A^{3/5} \tag{20}$$

The corona thickness in the starlike micelle determines the overall micelle radius and can be calculated by use of eq 12

$$L \sim aN_P^{3/5}(\gamma a^2/kT)^{6/25}N_A^{4/25}/\phi_s^{2/5} \tag{21}$$

The free energy of a chain in the micelle scales as

$$F_m/fkT \sim (\gamma a^2/kT)^{3/5}N_A^{2/5}\left\{\ln\left(\frac{N_P}{N_A^{5/9}f^{2/9}\phi_s^{2/3}}\right)\right\}^{2/5} \sim (\gamma a^2/kT)^{3/5}N_A^{2/5} \tag{22}$$

B. Critical Micelle Concentration. In order to calculate the critical micelle concentration (cmc) and the micellar phase chemical potential, we need to consider the grand canonical free energy:

$$\Omega = F_{\mathrm{m}} - f\mu_{\mathrm{ex}} \tag{23}$$

where μ_{ex} is the chemical potential of the free, unaggregated chains. We take as a reference state for P block that of P chains in infinite dilution in the given aqueous salt solution, and for the A block that of the molten state, as is implicitly assumed in the micelle calculation. The chemical potential of the free chains[1,3] is dominated by the chain entropy and the collapsed core–solvent interface:

$$\mu_{\mathrm{ex}} \sim kT \log \phi + \gamma a^2 N_{\mathrm{A}}^{2/3} \tag{24}$$

ϕ is the copolymer concentration. The critical micelle concentration is calculated by minimization of the grand canonical free energy at fixed chemical potential. Balancing the micelle energy (eq 22) with the free chain chemical potential we find that

$$\phi_{\mathrm{cmc}} \sim \exp\left\{(\gamma a^2/kT)^{3/5} N_{\mathrm{A}}^{2/5}\left\{\ln\left(\frac{N_{\mathrm{P}}}{N_{\mathrm{A}}^{5/9} f^{2/9} \phi_{\mathrm{s}}^{2/3}}\right)\right\}^{2/5} - (\gamma a^2/kT) N_{\mathrm{A}}^{2/3}\right\} \sim \exp\{(\gamma a^2/kT)^{3/5} N_{\mathrm{A}}^{2/5} - (\gamma a^2/kT) N_{\mathrm{A}}^{2/3}\} \tag{25}$$

and the chemical potential at the cmc is

$$\mu_{\mathrm{cmc}}/kT \sim (\gamma a^2/kT)^{3/5} N_{\mathrm{A}}^{2/5}\left\{\ln\left(\frac{N_{\mathrm{P}}}{N_{\mathrm{A}}^{5/9} f^{2/9} \phi_{\mathrm{s}}^{2/3}}\right)\right\}^{2/5} \sim (\gamma a^2/kT)^{3/5} N_{\mathrm{A}}^{2/5} \tag{26}$$

The aggregation number, cmc, and chemical potential of the micellar solution are dominated by the core block properties (γ, N_{A}) and are therefore identical, within a logarithmic factor, to those calculated for micelles of neutral diblock copolymers in a nonpolar, highly selective solvent.[1,4] Consequently, changes in salt concentration do not affect either the cmc or aggregation number, though the corona size decreases with increasing ϕ_{s}.

IV. Adsorption of Neutral–Charged Diblock Copolymers

Adsorption of diblock copolymers from a selective solvent onto a surface is a planar form of aggregation. As in micelles, the adsorbed film can be divided into two regions: a molten "core" film of A segments adsorbed on the surface, into which neither solvent nor P segments penetrate, and a solvated "corona" brush of the charged block, grafted to the surface via the adsorbed A film (see Figure 1). We assume there are no interactions (other than impenetrability) between the charged block and the surface.

Two forces control the interactions between A segments and the surface: surface energy, and long range interactions between surface, film, and solvent. The surface energy can be defined through a dimensionless spreading coefficient $S = \{\gamma_{\mathrm{ws}} - (\gamma + \gamma_{\mathrm{Aw}})\}a^2/kT$. γ_{ws} is the interfacial tension between the surface and the solvent, and γ_{Aw} between polymer A and the surface. As previously defined, γ is the interfacial tension between A and the solution. If S is positive, the A droplet will wet the surface, while a negative S indicates a nonwetting film. We assume that the long range interactions can be described in terms of van der Waals forces only. The energy of a uniform film (per unit area) is

$$F_{\mathrm{A}}/kT = -S + H/12\pi d^2 + \sigma(d^2/a^2 N_{\mathrm{A}}) \tag{27}$$

where H is the effective Hamaker constant for the A film, in contact on one side with the solid surface and on the other side with the solvent, and d is the A film thickness. The last term describes the elastic energy of the A chains, due to their stretching from the free chain dimension of $aN_{\mathrm{A}}^{1/2}$ to a height d. As in the previous section, we assume that there is no penetration of either P segments or solvent into the A film, so that d can be related to the surface density σ by $N_{\mathrm{A}}\sigma a/d \sim 1$.

The charged P block forms a swollen brush with surface density σ. When a^2/σ, the area per chain, is larger than the charged block radius of gyration, the chains do not interact. The adsorbed layer properties are then determined by the A block only, and resemble those of an adsorbed homopolymer A film. As the grafting density increases, the charged chains overlap and stretch in the direction normal to the surface, forming a solvated brush. The brush thickness and free energy can be described by eqs 7 and 8, so that the copolymer layer energy (per chain) scales as

$$F_{\mathrm{L}}/kT \sim -S/\sigma + \sigma^2 N_{\mathrm{A}} + H/(\sigma^3 N_{\mathrm{A}}^2) + N_{\mathrm{P}}\sigma^{5/6}/\phi_{\mathrm{s}}^{2/3} \tag{28}$$

For simplicity we neglect such contributions as the confinement energy of junction points, which is significant only for very short chains, or the line tension, which is negligible when the perimeter length is small compared to the surface area, namely, when the film area is large. Also, we discuss only the case of asymmetric copolymers, where $N_{\mathrm{P}} > N_{\mathrm{A}}$. The surface density of an adsorbed copolymer layer deposited onto the surface, in equilibrium with pure aqueous salt solutions, is obtained by minimization of the layer free energy with respect to the surface density

$$S + \frac{H}{(\sigma^2 N_{\mathrm{A}}^2)} \sim \sigma^3 N_{\mathrm{A}} + N_{\mathrm{P}}\sigma^{11/6}/\phi_{\mathrm{s}}^{2/3} \tag{29}$$

Considering only wetting films, where $S > 0$, we can distinguish between two regimes. The first occurs when the spreading coefficient is sufficiently high so that the van der Waals interactions can be neglected. The layer properties are then

$$\sigma \sim (S/N_{\mathrm{P}})^{6/11}\phi_{\mathrm{s}}^{4/11} \tag{30}$$

$$L \sim S^{2/11} N_{\mathrm{P}}^{9/11}/\phi_{\mathrm{s}}^{6/11} \tag{31}$$

In the second regime, long range interactions dominate the adsorbed block contribution (van der Waals regime), so that the surface density scales as

$$\sigma \sim (H/N_{\mathrm{P}})^{6/23}\phi_{\mathrm{s}}^{4/23}/N_{\mathrm{A}}^{12/23} \tag{32}$$

and the P brush thickness as

$$L \sim \frac{H^{2/23} N_{\mathrm{P}}^{21/23}}{\phi_{\mathrm{s}}^{14/23} N_{\mathrm{A}}^{4/23}} \tag{33}$$

In both regimes, the A block stretching energy is negligible. As could be expected, the surface density increases as a function of salt concentration, due to the increase in screening of electrostatic interactions. The brush thickness, though, decreases as a function of salt concentration. The dependence of both surface density and brush thickness on the molecular weight of the blocks and Hamaker constant is similar to those predicted for neutral copolymer adsorption under the same conditions[1] but differ from a mean field model of adsorbed neutral-charged layers.[9] The mean field approach predicts that, in the van der Waals regime, surface density increases with $\phi_s^{1/11}$, a much weaker dependence than the (4/23) power law of our scaling model.

In most systems, the adsorbing wall is in contact with a copolymer solution of finite concentration, acting as a reservoir. The reservoir chemical potential plays a significant role in determining adsorbed layer properties, and in turn depends on the bulk concentration of copolymer chains. Considering the grand canonical free energy, per unit area, of an adsorbed layer in equilibrium with a reservoir of chemical potential μ_{ex}

$$G = \sigma F_L - \mu_{ex}\sigma \tag{34}$$

The equilibrium surface density can be obtained by minimization of G at constant chemical potential

$$\mu_{ex}/kT \sim \sigma^2 N_A + N_P \sigma^{5/6}/\phi_s^{2/3} - H/(\sigma^3 N_A^2) \tag{35}$$

In dilute copolymer solutions, below the cmc, the chemical potential increases slowly as a function of copolymer concentration (see eq 24). The adsorbed layer energy dominates the grand canonical free energy, and the surface density is determined by a balance between the stretching energy of the charged block and the van der Waals interactions. Layer properties are, therefore, similar to those of a layer at equilibrium with pure aqueous solutions (eqs 32 and 33). When the bulk concentration exceeds the cmc, micelles begin to form, and the concentration of free chains is fairly constant. The solution chemical potential (neglecting micelle–micelle interactions and their translation energy) remains, therefore, unchanged at the cmc value of $\mu_{cmc}/kT \sim (\gamma a^2/kT)^{3/5} N_A^{2/5}$. The adsorbed layer free energy is dominated, to a large extent, by the charged block

$$\sigma \sim \gamma^{18/25} \phi_s^{4/5} N_A^{12/25}/N_P^{6/5} \tag{36}$$

$$L \sim \gamma^{6/25} N_P^{3/5} N_A^{4/25}/\phi_s^{2/5} \tag{37}$$

The dependence of surface density on the P block molecular weight and the salt concentration is much stronger than in a layer adsorbed from dilute solution: in the second case, σ is smaller by a factor $N_P^{36/55}$, or $N_P^{108/115}$, than that of an equivalent adsorbed layer as described by eqs 30 and 32, respectively. For high molecular weight chains this difference is significant. The effect of both N_P and σ on the brush thickness is weaker, though, than in the dilute solution adsorption.

V. Discussion

We have studied aggregation phenomena of asymmetric charged–neutral diblock copolymers in aqueous salt solutions, discussing solutions where salt concentration is such that the range of electrostatic interactions is smaller than that of excluded volume correlations. We adapt a scaling model to describe semidilute, charged chains under such conditions, and apply it to densely grafted chains where a brush is formed. Chain properties are calculated, for both planar and spherical (starlike) surfaces, as a function of surface density (or number of star chains), chain molecular weight, N, and the solution salt concentration, ϕ_s.

We find that the N and σ (or f) power laws governing chain dimensions and free energy are the same as in a neutral brush in a nonpolar, good solvent.[2,5,6,13] The similarity in the scaling of free energy with surface density, between charged and neutral planar brushes, has also been noted in a self-consistent field (SCF) model.[14] In the concentration range where our model applies, the SCF model power law dependence of the brush thickness on σ is approximately 1/3, as in the neutral brush. The free energy of the planar brush and the brush thickness in both geometries strongly decrease with salt concentration, due to the increase in electrostatic interaction screening. However, the rapid decay in segment concentration in the spherical brush contributes to diminish the electrostatic interactions between neighboring segments more effectively than screening by the solution counterions so that the spherical brush free energy is nearly independent of ϕ_s. Charged chains, therefore, prefer interface curvature more strongly than their neutral counterparts.

Diblock copolymers aggregate to form micelles in a selective solvent. The micellar phase is characterized by the aggregation number f, the micelle concentration threshold (cmc), micelle size, and the phase chemical potential. We find that the phase properties of charged–neutral copolymer micelles are dominated by the neutral core block, so that the cmc, f, and the chemical potential are similar (within a logarithmic factor) to those of neutral copolymer micelles in a nonpolar selective solvent.[14] The charged chains in the corona, though, are stretched compared to their neutral counterparts, so that the overall micelle size is larger. The similarity between charged and neutral copolymer micelles is not surprising since, under the constraints we impose on ϕ_s and copolymer asymmetry, the corona block free energy is nearly independent of both molecular weight or salt concentration. Obviously, in extremely dilute salt solutions where electrostatic correlations and not excluded volume interactions dominate, the micellar phase properties would be determined by the charged block and the electrostatic interactions between neighboring chains.[3] For the asymmetric copolymers discussed in this study, the electrostatic repulsion between neighboring charged blocks would overshadow the neutral block interfacial energy, so that the driving force to aggregation would become negligible. Micellization would probably not take place at all under such conditions.

The second form of aggregation examined was that of adsorption from a selective solvent onto a planar surface. Layers adsorbed from extremely dilute copolymer solutions are controlled by a balance between the charged block energy and van der Waals interactions of the neutral block. Layer surface density decreases with N_P and increases with the solution salt concentration. The overlap surface density of the charged block, σ^*, scales as $a^2 R_g^2 \sim \phi_s^{-4/5} N_P^{-6/5}$. It is much lower than the adsorbed layer surface density, ensuring the validity of the strong stretching assumption inherent in our model. Examining the equilibrium between an adsorbed layer and a micellar solution, we find that the layer properties are determined by a balance between micellar solution, we find that the layer properties are determined by a balance between micellar phase potential and the charged block stretching energy. The surface density is much lower, in this case, than in adsorption from dilute copolymer solutions (though still higher than σ^*), due to the competition between micellization and adsorption on the surface. The thickness of the charged brush is the same as the micelle corona, though the surface density of the micelle, which scales as $f(a/R_{core})^2 \sim (\gamma a^2/kT)^{2/5}/N_A^{2/5}$, is quite higher than that of the adsorbed layer. This could be attributed to the dominance of the charged block stretching energy: in micelles, chain stretching is alleviated by the increase in volume as a function of radius, thereby allowing higher surface densities. In the planar adsorbed layer configuration such relaxation is not possible.

It should be noted than in this analysis we neglect the insolubility of the charged block organic backbone in the aqueous solution. In a recent paper, Ross and Pincus[8] find a first-order conformational phase transition for planar (and second order for curved) brushes, in which a charged brush collapses at certain grafting densities and fairly low charge density along the backbone, in the absence of added salt. However, in the case of highly charged chains discussed in this paper, where every segment is assumed to carry an ionic unit, this collapse should not occur.

Light scattering and sedimentation experiments on the micellization of neutral–highly charged block copolymers[15–17] have shown that the aggregation number decreased only slightly with an order of magnitude increase in the charged block molecular weight but increased significantly with slight increases in neutral chain molecular weight. The condition of having the electrostatic persistence length, b, shorter than the blob size, ξ, is easy to achieve in aqueous salt solutions of polyelectrolytes. This is in qualitative agreement with the predictions of eq 19. The cmc was found to decrease with salt concentration, up to a point beyond which variation in salt concentration had no further affect. As the core block molecular weight was increased, the cmc was less and less effected by changes in the salt concentration. Examination of eq 25 shows that increasing either the salt concentration or N_A decreases the value of the first term in the exponential, so that the cmc decreases. At high N_A or ϕ_s values the first term is negligible, and the cmc is unaffected by any further changes in the salt concentration. The system investigated was that of styrene–(quarternized) vinyl pyridine in mixtures of water, methanol, and LiBr. It is not clear how the solution composition, namely, the ratio of water to methanol, may have affected the micelle characteristics, so that quantitative verification is impossible. In recent experiments, the effect of salt concentration on micelle properties was examined using dynamic and static light scattering.[18,19] The system examined was of diblock *tert*-butylstyrene/styrenesulfonate copolymers in aqueous solutions of sodium chloride. The aggregation number did not change significantly over a salt concentration range of 3 orders of magnitude, in agreement with the predictions of eq 19. The changes in the micelle hydrodynamic radius, however, did not fit a power law form as suggested by eq 21. This incompatibility may be due to the small number of data points, taken over a range of salt concentration which may also include the high and low salt regimes (which this paper does not discuss). More scattering experiments, measuring the micelle size, aggregate molecular weight, and cmc of charged–neutral copolymers in various salt concentrations should enable a more detailed examination of these model predictions.

The properties of adsorbed charged–neutral block copolymers in aqueous salt solutions[20] have not been extensively studied, so far. There is some evidence[18] that the adsorbed brush thickness decreases with salt concentration, but surface heterogeneities preclude direct comparison with these model predictions.

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