Macromolecules 1993, *26*, 2691-2697

Charged Diblock Copolymers at Interfaces

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Received October 21, 1992; Revised Manuscript Received February 12, 1993

ABSTRACT: We discuss the interfacial behavior of diblock copolymers where one of the blocks is a weakly charged polyelectrolyte and the other block is an organic polymer insoluble in water. In solution in water, for a fixed composition, the copolymer forms spherical micelles if the fraction of charged monomers is smaller than a critical value. From a micellar solution, charged copolymers can adsorb at both an air–water and a solid–water interface. However in both cases, strong adsorption and the formation of a dense polyelectrolyte grafted layer (brush) is possible only if the electrical charge is small enough. The adsorption isotherm reaches a plateau when the concentration is raised above the critical micellar concentration where the energetic properties of the layer are dominated by the neutral sequence. The value of the surface excess on the plateau increases with the fraction of charged monomers. For an adsorption at the oil–water interface, we predict a finite range of parameters (molecular weight and electric charge) for which the Schulman condition can be satisfied so that the interfacial tension between oil and water vanishes in the presence of copolymer; the interface is then unstable, and oil is dissolved in water.

I. Introduction

In many aspects, diblock copolymers can be considered as the macromolecular analogues of simple surfactants.[1] In solution both in a monomeric and a polymeric solvent, they self-assemble to form a broad variety of mesophases[2] ranging from spherical or cylindrical micelles to lamellar or ordered cubic phases. They also are surface active materials which accumulate at interfaces and lower interfacial tensions.[3] These properties are used in various applications such as the compatibilization of polymer blends or the stabilization of colloidal suspensions.[4]

From a theoretical point of view, the whole body of statistical and scaling theories that has been developed for homopolymer solutions and melts can be extended to diblock copolymers. This makes them amenable to a rather simple theoretical description which can then often be used as a guideline for the properties of simple surfactant molecules.[5]

In this context, the adsorption of neutral diblock copolymers in a selective solvent onto a solid surface has been recently studied both theoretically and experimentally.[6,7] A thick adsorption layer builds up with a double-layer structure: the insoluble block anchors the chains on the surface and forms a thin dense film; the soluble block forms a so-called polymer brush dangling into the solvent where the chains are extended. The characteristics of this layer are governed by the nature of the organization of the bulk solution (the type of mesophase formed), the direct long-range molecular interactions between the insoluble monomers and the adsorbing surface (van der Waals interactions), and the elasticity of the polymers in the grafted polymer brush. Due to the large thicknesses of polymer brushes, much larger than the natural radius of the soluble blocks in solution, the coating of colloidal particles with neutral diblock copolymers turns out to be a very efficient way to stabilize suspensions.

The macromolecular analogue of an ionic surfactant is a charged diblock copolymer comprising a polyelectrolyte sequence A containing N_A monomers, a fraction f of these being charged, and a neutral sequence B containing N_B organic monomers insoluble in water. The aim of the present paper is to study theoretically the surface properties of these copolymers at both an oil–water and a solid–water interface.

The copolymers are assumed to be soluble in water where they form a micellar solution but to be insoluble in oil. At the oil–water interface the diblock copolymers assemble, their junction points lie on the interface, and each sequence is dissolved in one of the solvents. The copolymer is a good surfactant if the lowering of the surface tension is large, i.e. if the number of adsorbed chains per unit area is large. We thus look *for the conditions of formation of* a dense brush on the surface. At the solid–water interface, the structure of the adsorbed charged copolymer layer is very similar to that of neutral copolymers. Here also for colloid stabilization purposes, we require a thick layer and thus a dense polymer brush.

The paper is organized as follows. In the next section we study micelle formation by charged diblock copolymers in water along the lines of ref 8. The properties of charged polymeric brushes obtained by Pincus[9] are rederived in section III using a simplified "box model". The copolymer adsorption at an oil–water and at a solid–water interface is discussed in section IV. The last section presents our conclusions and gives some possible issues.

II. Micellar Solutions

At extremely low concentrations, charged diblock copolymers do not aggregate in water and form a homogeneous solution. The insoluble B block of the copolymer collapses; we consider here the limit where water is such a poor solvent that the B monomers form dense molten globules from which both water and the charged block A are excluded. The radius of the globules is then the compact radius $R_B = N_B^{1/3}a$, a being the monomer size. If we take as a reference state for the B monomers the molten state, the free energy E_B of the collapsed block is dominated by the surface tension γ_B between the solvent and a B melt.

$$E_B = 4\pi\gamma_B R_B^{\,2} \sim N_B^{\,2/3} \tag{1}$$

The A block has the conformation of an isolated polyelectrolyte chain in a dilute solution. Its radius R_A and free energy E_A can be calculated via a Flory argument.[10] Ignoring excluded volume interactions and assuming thus that water is a Θ solvent, the Flory free energy is the sum of an elastic and an electrostatic contribution.

$$E_A/kT = R_A^{\,2}/N_A a^2 + l_B (fN_A)^2/R_A$$

In this free energy, the size of an A monomer has been chosen for simplicity equal to that of a B monomer. The

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electrostatic free energy has been scaled by the thermal excitation kT; this defines the Bjerrum length $l_B = e^2/4\pi\epsilon kT$ where e is the monomer charge and ϵ is the dielectric constant of water. The Bjerrum length is equal to 7 Å and is of the order of the monomer size a. Here and in the following, the discussion is at the level of scaling laws and numerical constants of order unity are thus ignored. The minimization of E_A gives a radius increasing linearly with the molecular weight $R_A \sim N_A f^{2/3}(a^2 l_B)^{1/3}$ and the free energy of the A block

$$E_A = kTN_A f^{4/3}(l_B/a)^{2/3} \qquad (2)$$

These expressions are meaningful only if the radius R_A is larger than the Gaussian radius of the A block i.e. if the charge fraction is large enough $f > f_{\text{Gauss}} = N_A^{-3/4}(l_B/a)^{1/2}$. In the remainder of the paper we suppose that this condition is fulfilled; in the reverse limit, the electrostatic interactions do not play any role and the polymer statistics remain Gaussian.

The chemical potential of a charged copolymer chain in an extremely dilute solution of concentration ϕ (measured as a number of chains per unit volume) can then be written as

$$\mu_{sc} = kT \log \phi + E_A + E_B \qquad (3)$$

The first term is the translational entropy. Notice that we have ignored here the contribution to the chemical potential of the counterions; in the weak charge limit ($f < 1$) they do not condense on the polymer and they are uniformly distributed throughout the solution, our reference state is thus an ideal gas of counterions of concentration $\rho = fN_A\phi$.

As the copolymer concentration is increased, the chains start to aggregate and form micelles at a well-defined concentration ϕ_{cmc}. The structure and stability of the micelles has been studied by Marko and Rabin.[8]

Following their work, we consider a solution with a given chemical potential μ (or equivalently a given chain concentration) where one spherical micelle has formed and we discuss the stability of the micelle. The micelle has a dense core formed by molten B monomers. If the B melt is incompressible, the radius of the core R_c is related to the aggregation number p by $R_c = a(3pN_B/4\pi)^{1/3}$. The charged A chains form a corona of radius R_m around the core. For the sake of simplicity we consider here only diblock copolymers forming starlike micelles such that $R_m \gg R_c$. It can be checked a posteriori that it is the case if the charged sequence is long enough $N_A > N_B^{2/3}$. Marko and Rabin have also shown that no counterion condensation occurs in this case.

The thermodynamic potential that governs the stability of the micelle is the grand canonical free energy

$$\Omega = F_A + F_B - \mu p \qquad (4)$$

The free energy of the core F_B is dominanted by the surface tension contribution

$$F_B = 4\pi\gamma_B R_c^{\,2}$$

The free energy of the corona is the sum of an electrostatic and an elastic contribution

$$F_A/kT = pR_m^{\,2}/N_A a^2 + l_B(fpNA)^2/R_m$$

The equilibrium structure of the micelle is found by minimizing the free energy Ω, and the micelle is stable if the free energy Ω is negative. The critical micellar concentration is thus the concentration where Ω is minimal and vanishes. The value of the solution chemical potential where this occurs is then obtained from eq 4.[8]

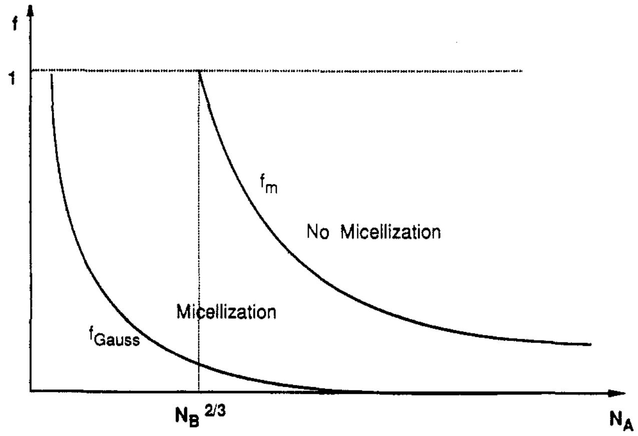


Figure 1. Partial phase diagram of charged diblock copolymer solutions. Only copolymers such that $f > f_{\text{Gauss}} = N_A^{-3/4}(l_B/a)^{1/2}$ and $N_A > N_B^{2/3}$ are considered.

$$\mu_{\text{cmc}} = (E_A E_B^{\,2})^{1/3} \sim N_A^{\,1/3} N_B^{\,4/9} f^{4/9} \qquad (5)$$

The aggregation number at the cmc is

$$p = E_B/E_A \sim N_B^{\,2/3}/N_A f^{4/3} \qquad (6)$$

The size of the micelle is approximately equal to the size of the corona $R_m = R_A p^{1/3}$.

Micelles actually form only if the aggregation number p is larger than unity, i.e. if the fraction of charged A monomers is small enough

$$f < f_m = (\gamma_B a^2/kT)^{3/4}(a/l_B)^{1/2} N_B^{\,1/2} N_A^{\,-3/4} \qquad (7)$$

If the fraction of charged A monomers is larger than f_m, the electrostatic interaction is too strong to allow the formation of aggregates and the chemical potential of the copolymer solution is given by eq 3.

If the charge fraction is smaller than f_m the critical micellar concentration is of order $\phi_{\text{cmc}} \sim \exp[-\{E_A + E_B - \mu_{\text{cmc}}\}]/kT$. Above the critical micellar concentration, the concentration of nonaggregated copolymer chains remains approximately equal to ϕ_{cmc} and the structure of the micelles remains that at the cmc. In particular the chemical potential of the solution is given by eq 5 if we ignore a small logarithmic correction due to the translational entropy of the micelles.[11] Notice however that our reference state for the chemical potential includes the translational entropy of the counterions which increases with the chain concentration. A partial phase diagram of the charged diblock copolymer solution summarizing these results is given in Figure 1 for a fixed value of N_B in a plane f–N_A.

III. Charged Polymeric Brushes

When the micellar solution in water is in contact with an interface, the block copolymer adsorbs and eventually forms a polyelectrolyte brush in water. The junction points of the copolymer are trapped at the interface, and the charged blocks stretch toward the water solution. The number of adsorbed copolymer chains per unit area is governed by the conformational characteristics of the neutral block and is discussed in section IV below. Here, we do not consider the neutral sequence of the copolymer and we assume that the surface concentration of adsorbed chains is imposed in order to study the properties of the polyelectrolyte grafted layer.[12] Most of the scaling results have already been obtained by Pincus[9] or Borisov et al.;[13] we rederive them here using an extremely simplified description of the electrostatics that we call the box model.

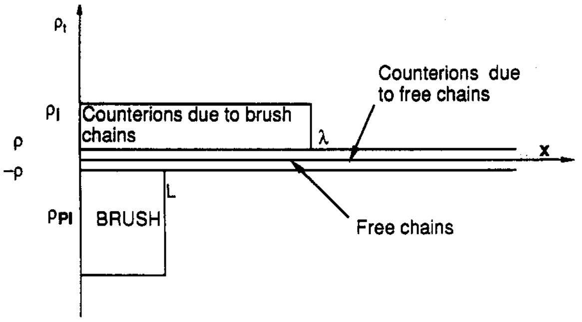


Figure 2. Box model. The figure shows the densities of positively charged (counterions) and negatively charged (copolymer) ions.

The bulk of the solution is a micellar solution where the total number of copolymer chains per unit volume is ϕ, and the concentration of counterions is then $\rho = \phi f N_A$. As the screening of the electrostatic interactions is essentially due to the counterions, for the study of electrostatic properties we replace the copolymers by a uniform rigid background of charge density ρ. The relevant Debye–Hückel screening length κ^{-1} is then given by[14]

$$\kappa^2 = 4\pi\rho l_B = 4\pi\phi f N_A l_B \tag{8}$$

In the box model, we ignore the detailed variation of the concentrations of monomers and counterions and replace them by constants over certain regions. The monomer concentration in the adsorbed layer is constant over the thickness L of the layer. If the grafting density is σ, the monomer concentration is $\sigma N_A/L + N_A\phi$ and the charge density due to the polyelectrolyte is $\rho + \sigma f N_A/L$. The extra surface charge per unit are due to the adsorption $\sigma f N_A$ defines a so-called Gouy–Chapman length[14,15]

$$\xi = (2\pi l_B N_A f \sigma)^{-1} \tag{9}$$

The Gouy–Chapman length is the size of the region over which the counterions are confined close to a surface carrying a surface charge density $\sigma f N_A$ equal to that of the grafted layer but localized on the surface, in the absence of external salt.

The counterions of the adsorbed polyelectrolyte are confined in the vicinity of the interface over a thickness λ. In the region of size λ close to the interface the counterion density is $\rho + \rho_i$ where $\rho_i = \sigma f N_A/\lambda$. Outside this confinement region the counterion concentration has the bulk value ρ.

The charge densities due to the polymer (negative charges) and to the counterions (positive charges) are represented on Figure 2.[16]

The total electrostatic contribution to the free energy per unit area of the adsorbed polyelectrolyte layer is the sum of the translational entropy of the ideal gas of counterions F_t and of the direct electrostatic term F_{el}. Within the box model both terms are easily estimated. Taking as a reference state the bulk counterions, the translational entropy reads

$$F_t/kT = \lambda(\rho + \rho_i)\log(1 + \rho_i/\rho) - \sigma f N_A \tag{10}$$

The electric field E in the z direction is related to charge density by the Gauss law. The direct electrostatic contribution is obtained by integration of the free energy density $^1/_2\epsilon E^2$

$$F_{el}/kT = 2\pi l_B L(\sigma f N_A)^2(L/\lambda + \lambda/L - 2)/3 \tag{11}$$

Notice that this formula neglects any image charge effects that might arise at the interface between water with a high dielectric constant and a medium of lower dielectric constant (such as oil). As shown in the Appendix, these effects can be neglected as long as the adsorbed chains do not form a two-dimensional dilute solution.

The total free energy of the adsorbed layer is obtained by adding to the electrostatic terms the stretching free energy of the polyelectrolyte block of the copolymer

$$F_s/kT = {}^3/_2 L^2\sigma/N_A a^2 \tag{12}$$

The equilibrium structure of the polyelectrolyte brush is then obtained by minimization of the total free energy $F_A = F_t + F_{el} + F_s$ with respect to both L and λ. We now discuss this structure in various regimes corresponding to the relative values of the three length ξ, κ^{-1}, and L.

(i) If the counterion concentration ρ_i in the brush is larger than the bulk counterion concentration ρ, the Debye–Hückel screening length κ^{-1} is the largest of the three lengths and the external solution plays no role in the properties of the grafted layer. Two limits must then be distinguished: the strong charging limit when L is larger than ξ corresponding to large grafting densities σ and the weak charging limit when L is smaller than ξ corresponding to small grafting densities.

In the strong charging limit the counterions of the adsorbed chains are trapped inside the brush and the length λ is equal to the brush height L. The equilibrium brush height is

$$L = 3^{-1/2} a N_A f^{1/2} \tag{13}$$

The swelling of the brush is essentially due to the osmotic pressure of the counterions, and as noted by Pincus, the brush height does not depend on the strength of the electrostatic interaction measured here by l_B. The contribution of the charged A block to the chemical potential of the adsorbed copolymer is also dominated by the translational entropy of the counterions

$$\mu_A/kT = \frac{\partial F_A/kT}{\partial\sigma} = N_A f\log(\rho_i/\rho) = N_A f\log(\sigma f^{1/2}/\rho a) \tag{14}$$

In the weak charging limit, the brush height is small and as far as the electrostatic calculations are concerned, the copolymer charges can be considered as localized on the surface, the counterions are then confined within the Gouy–Chapman length $\lambda = 3\xi$. The brush height is

$$L = 4\pi/9 l_B N_A{}^3 f^2 \sigma a^2 \tag{15}$$

The chemical potential is also dominated by the translational entropy of the counterions

$$\mu_A/kT = N_A f\log(\rho_i/\rho) = N_A f\log[(N_A f\sigma)^2 l_B/\rho] \tag{16}$$

The crossover between the weak charging and the strong charging limits occurs when $\sigma = \sigma_1 \sim 1/(N_A{}^2 f^{3/2} l_B a)$. All these results obtained from the box model are identical within numerical prefactors of order unity to those obtained from a more complete solution of the Poisson–Boltzmann equation by Pincus.

(ii) In the opposite limit where the counterion density due to the grafted chains ρ_i is smaller than the bulk value ρ, the Gouy–Chapman length ξ is the largest length of the problem and the bulk counterions screen the electrostatic interactions. Two limits must also be considered, the weak screening limit when the Debye–Hückel screening length κ^{-1} is larger than the brush height L and the strong screening limit if $\kappa L \gg 1$.

In the weak screening limit, the counterions are confined within a screening length and $\lambda = \kappa^{-1}$. The height of the brush has approximately the same value as in the weak charging limit (eq 15); the chemical potential of an

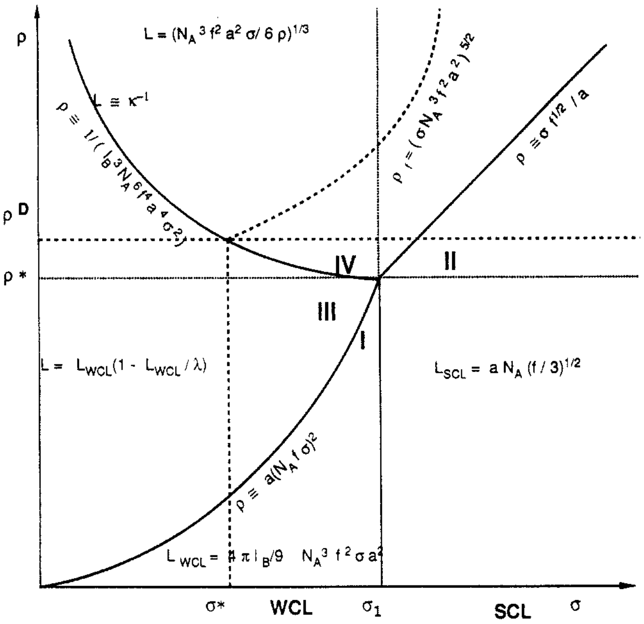


Figure 3. Diagram of states of a polyelectrolyte brush. The four regimes are the weakly charged brush (I), the strongly charged brush (II), the weak screening regime (III), and the strong screening regime (IV).

adsorbed chain is dominated by the translational entropy of the counterions

$$\mu_A/kT = (N_Af)^2\sigma(12\pi l_B/\rho)^{1/2}$$

The crossover toward the weak charging limit occurs for $\rho = (\sigma N_Af)^2 l_B$.

In the strong screening limit, the counterions are confined inside the brush and $\lambda = L$. The height of the brush is given by

$$L \sim N_Af^{2/3}(\sigma a^2/\rho)^{1/3}$$

The chemical potential is

$$\mu_A/kT \sim N_A(f^2\sigma/a\rho)^{2/3}$$

The crossover toward the weak screening limit occurs when $\rho = 1/(l_B{}^3a^4f^4N_A{}^6\sigma^2)$ and the crossover toward the strong charging limit when $\rho = \sigma f^{1/2}/a$. A more detailed theory for these two regimes where screening is important can be made using the Debye–Hückel equation; as above, it gives the same rsults as the box model within numerical factors of order unity.

The various regimes for the charged polymer brush are summarized on Figure 3. The adsorbed polymer layer indeed forms a brush if the grafting density is large enough that neighboring chains overlap, i.e. if $\sigma > \sigma^* = 1/L^{-2}$; at low concentrations of counterions ρ in the bulk $\sigma^* = 1/(N_A{}^2f^{4/3}l_B{}^{2/3}a^{4/3})$, and at higher values of ρ, $\sigma^* = \rho^{2/5}/(N_A{}^{6/5}f^{4/5}a^{4/5})$. At lower grafting density ($\sigma < \sigma^*$) the adsorbed chains interact only very weakly and their radius is that of isolated chains in the bulk. In the following we consider only true polyelectrolyte brushes at low bulk copolymer concentration. We thus only deal with the strong and weak charging limits; however the full diagram would be useful if salt were added to the copolymer solution. The behavior of the polyelectrolyte grafted layer is then the same as that presented here, but the counterion concentration in the bulk must be replaced by the total concentration of free ions $2n$ where n is the salt concentration.

IV. Copolymer Adsorption

We now use the results of the two previous sections to discuss the adsorption of charged diblock copolymers either at an oil–water interface or at a solid–water interface. We assume throughout this section that the adsorption is an equilibrium process even though the potential barriers against adsorption are large especially in the early stages (because of the image charges discussed in the Appendix) and thus the adsorption kinetics is expected to be very slow.

The bulk copolymer solution is in a micellar phase and the chemical potential of the copolymer chains is given by eq 5. The chemical potential of the adsorbed chains μ is the sum of the contributions of the two blocks $\mu = \mu_A + \mu_B$. The chemical potential of the neutral B block depends on the problem considered and is discussed below. The chemical potential of the charged A block is always dominated by the entropy of the counterions as discussed above and in all the regimes $\mu_A/kT = N_Af \log(1 + \rho_i/\rho)$. The balance of chemical potential can thus be written as

$$kTN_Af \log(1 + \rho_i/\rho) + \mu_B = \mu_{cmc} \qquad (17)$$

We are here interested in the strong adsorption limit; i.e. we want to investigate the possibility of formation of polyelectrolyte brushes. As we consider only very dilute copolymer concentrations, the only regimes of interest for the adsorbed layer are the weak charging and strong charging regimes of Figure 3. In these limits, the concentration of counterions trapped in the adsorbed layer is much larger than the concentration of free counterions in the bulk $\rho_i/\rho \gg 1$. In both cases, if $\mu_B > 0$, this requires that the chemical potential μ_{cmc} is larger than kTN_Af. Equation 5 imposes then that strong adsorption is possible only if

$$f < f_a = N_B{}^{4/5}N_A{}^{-6/5}(\gamma_Ba^2/kT)^{6/5}(l_B/a)^{2/5} \qquad (18)$$

In the range of molecular weights considered ($N_A > N_B{}^{2/3}$), this value of the charge fraction is smaller than the value f_m below which micelles form given by eq 7. One can also check directly that in the case where no micellization is possible ($f > f_m$), the adsorption is always weak as long as the bulk copolymer concentration is dilute. Equation 18 is one of the essential results of this paper, a charged diblock copolymer is a good surfactant (forming micelles and assembling at interfaces) only if the fraction of monomers that carry a charge in the water-soluble block is small enough. If f is too large, i.e. if the energy penalty associated with the aggregation of the charges in micelles or adsorbed layers is too high, the charged diblock copolymer is highly soluble in water and does not have any surface activity. We now study in more detail the adsorption in the two cases of interest in the limit where the charge fraction is smaller than the critical value f_a.

1. Adsorption at an Oil–Water Interface. At an oil–water interface, a charged diblock copolymer builds up a double-brush structure where the neutral block forms a usual polymer brush on the oil side of the interface, the junction point lies exactly at the interface, and the charged A block forms a polyelectrolyte brush on the water side.

The chemical potential of the neutral block is then given in a first approximation by the Alexander scaling theory of neutral brushes in a good solvent.[17]

$$\mu_B/kT = -N_B\Delta\chi + N_B(\sigma a^2)^{5/6} \qquad (19)$$

The second term is the stretching energy of the polymers in the brush, the first term describes the change in the interaction between each monomer and its environment, and $\Delta\chi$ is the change in the Flory interaction parameter between the bulk state and the oil solvent. For simplicity, in the following we consider only an athermal solvent for which $\Delta\chi = 0$. Positive values of $\Delta\chi$ strongly favor adsorption even in the absence of micellization; however if $\Delta\chi$ is too large the copolymer becomes soluble in oil. Negative values of $\Delta\chi$ reduce the adsorption.

If the bulk concentration is large enough, the chemical potential of the grafted layer is dominated by the neutral block of the copolymer and the grafting density reaches a pseudoplateau

$$\sigma_p = a^{-2}N_B^{-2/3}N_A^{2/5}f^{8/15}(\gamma_B a^2/kT)^{4/5}(l_B/a)^{4/15} \quad (20)$$

In the range of parameters considered ($f > N_A^{-3/4}$, $N_A \gg N_B^{2/3}$) one can check that both on the oil side and on the water side the copolymer indeed forms a brush: for the neutral block, $\sigma_p \gg \sigma^* = 1/R_F^2$ where $R_F = N_B^{3/5}$ is the Flory radius of the B block; for the charged block $\sigma_p \gg \sigma^* = 1(N_A^2 f^{4/3} l_B^{2/3} a^{4/3})$. However the polyelectrolyte brush can be in the weak charging regime (if f and N_A are small enough) or in the strong charging regime (in most of the range of f and N_A).

The unexpected feature of the plateau value of the grafting density is its increase with both the fraction of charges and the molecular weight of the polyelectrolyte block. This is due to the fact that the chemical potential at the critical micellar concentration increases with f and N_A and that the chemical potential of the adsorbed layer does not depend on electrostatics but is dominated by the neutral block.

At very low copolymer bulk concentration ($\rho_{cmc} < \rho < a^{-3}\exp[-\{\mu_{cmc}/(N_A f kT)\}]$) the grafting density increases very rapidly with ρ (or ϕ). In the weak charging regime ($\sigma < \sigma_1$) it increases as

$$\sigma = 1/N_A f(\rho/l_B)^{1/2}\exp\{\mu_{cmc}/(2N_A f kT)\} \quad (21)$$

and in the strong charging limit ($\sigma > \sigma_1$)

$$\sigma = f^{-1/2}\rho a\exp\{\mu_{cmc}/(N_A f kT)\} \quad (22)$$

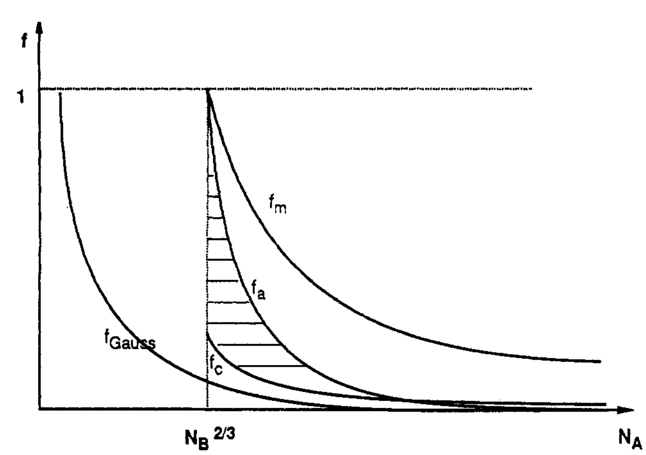
At an oil–water interface, the quantity of experimental relevance is the interfacial tension between oil and water that we write $\gamma = \gamma_0 - \pi$ where γ_0 is the interfacial tension of a bare oil–water interface and π the surface pressure of the copolymer.[18] The surface pressure of the copolymer has a contribution from the charged block dominated by the counterions ($\pi_A = kT\sigma N_A f$ in the strong charging limit and $\pi_A = 2kT\sigma N_A f$ in the weak charging limit) and a contribution due to the neutral block which in the Alexander model of polymer brushes is written as $\pi_B = kTa^{-2}N_B(\sigma a^2)^{11/6}$. Like for the chemical potential, the surface pressure is dominated by the neutral block of the copolymer. On the plateau of the adsorption isotherm, the surface pressure of the copolymer is thus

$$\pi = kTa^{-2}N_B^{-2/9}N_A^{11/15}f^{44/45}(\gamma_B a^2/kT)^{44/30}(l_B/a)^{22/45} \quad (23)$$

The surface pressure can be larger than the bare oil–water interfacial tension if the charge fraction f is large enough

$$f > f_c = N_B^{5/22}N_A^{-3/4}(l_B/a)^{-1/2}(\gamma_B a^2/kT)^{-3/2}(\gamma_0 a^2/kT)^{45/44} \quad (24)$$

Equations 18 and 24 define a range of values of the charge fraction f and of the molecular weight of the charged block N_A where, upon adsorption of the charged diblock copolymer at the oil–water interface, the oil–water interfacial tension can become negative and thus the interface between oil and water becomes unstable. This is shown on Figure 4. For such copolymers, the adsorption plateau given by (20) is not reached, the adsorption at the oil–water interface saturates when the interfacial tension vanishes, i.e. when $\sigma = a^{-2}(\gamma_0 a^2/kTN_B)^{6/11}$. At higher copolymer concentrations, the grafting density remains fixed at this value and the adsorption of the copolymer provokes the dissolution of the oil in water. As the bending energies of grafted copolymer layers are very high, one cannot expect the stable phase to be a stable bicontinuous microemulsion phase but rather a lamellar phase with alternating slabs of oil and water or an emulsion of oil in water.[19]



$$f_{Gauss} \cong (a/l_B)^{1/2}/N_A^{3/4}$$
$$f_m \cong (\gamma_B a^2/kT)^{3/4}(a/l_B)^{1/2}N_B^{1/2}/N_A^{3/4}$$
$$f_a \cong (\gamma_B a^2/kT)^{6/5}(a/l_B)^{2/5}N_B^{4/5}/N_A^{6/5}$$
$$f_c \cong (\gamma_B a^2/kT)^{-3/2}(\gamma_0 a^2/kT)^{45/44}(a/l_B)^{1/2}N_B^{5/22}/N_A^{3/4}$$

Figure 4. Schulman condition. The diagram shows the range of parameters in the f–N_A plane where the oil–water interfacial tension can vanish.

2. Adsorption at a Solid–Water Interface. If the B block of the copolymer completely wets the solid–water interface, i.e. if the spreading tension S of the B polymer melt is positive, the adsorbed block copolymer forms a double-layer structure with a continuous molten B film of thickness d in contact with the solid and a polyelectrolyte brush dangling into the solvent. The molten film is in a first approximation incompressible and its thickness d is related to the chain grafting density σ by $\sigma = a^{-3}d/N_B$.

As discussed in refs 6 and 7 for neutral diblock copolymers, the free energy per unit are of the B film is the sum of the stretching energy of the chains and of a molecular contribution $P(d)$. Following this work we take as an example of the molecular interaction a repulsive nonretarded van der Waals interaction $P(d) = A/12\pi d^2$ where the Hamaker constant A is positive.[11]

The chemical potential of the B block is then written as

$$\mu_B = kTd^2/N_B a^2 - AN_B a^3/6\pi d^3 \quad (25)$$

The equilibrium grafting density σ is given by the chemical potential balance of eq 17

$$\mu_{cmc}/kT + A/(kT6\pi N_B^2\sigma^3 a^6) = N_A f\log(1 + \rho_i/\rho) + N_B(\sigma a^2)^2 \quad (26)$$

When the chemical potential at the cmc is larger than $N_A f$, the van der Waals interaction is negligible. At low bulk concentration ($\rho_{cmc} < \rho < \exp[-\{\mu_{cmc}/(N_A f kT)\}]$) the grafting density is given by (21) and (22), at higher copolymer concentrations it reaches a plateau

$$\sigma_p = a^{-2}N_B^{-5/18}N_A^{1/6}f^{2/9}(\gamma_B a^2/kT)^{1/3}(l_B/a)^{1/9} \quad (27)$$

One can directly check that the adsorbed layer is actually a polymer brush ($\sigma_p > \sigma^*$) in the strong charging regime ($\sigma_p > \sigma_1$).

Because of the negative contribution to the chemical potential μ_B due to the van der Waals forces, adsorption of the copolymer can also occur if $\mu_{cmc} < N_Af$ but the grafting densities obtained are then much smaller.

V. Conclusions

We have discussed the adsorption of diblock copolymers made of an electrically charged block and a neutral block at the interface between either water and oil or water and a solid surface. Our essential result is that upon adsorption such copolymers can form a dense polyelectrolyte brush but only if the fraction of charged monomers in the polyelectrolyte block is smaller than a critical value given by (18). If the charge fraction is larger than this critical value, the osmotic pressure in the adsorbed layer is too large and the copolymer does not adsorb (or only weakly adsorbs). In other words, if the charge is too large, the charged copolymer is not a good surfactant, it does not form micelles and it is not surface active.

We also have shown that if the charge fraction and the degree of polymerization of the charged block are small enough the charged diblock copolymer can satisfy the Schulman condition at an oil–water interface,[20] i.e. that the interfacial tension of the oil–water interface with adsorbed surfactant can vanish. The interface is then unstable, and oil is dissolved in water. We have not discussed the precise phase diagram, but in view of the high value of the bending energy of the copolymer, we suggest that a lamellar phase or an emulsion phase is formed.

Our results are relevant for two types of experiments. At an oil–water interface one could measure the interfacial tension and deduce the copolymer adsorbed amount. Such experiments have been done in Strasbourg[21] where the reduction of the interfacial tension due to the adsorbed copolymer was found rather weak. This is perhaps due to a too high value of the fraction of charged monomers.

The adsorption behavior of charged diblock copolymers has also been studied recently with a surface force apparatus.[22] Direct adsorption of the polyelectrolyte never was possible in the absence of salt. The polyelectrolyte brush was prepared at very high ionic strength and then the solvent was replaced by pure water. Our calculations suggest that direct adsorption could be possible by lowering the charge fraction if the neutral block completely wets the mica substrate.

The major limitation of this work is the assumption that the bulk and the surface are at thermodynamic equilibrium. There are however enormous potential barriers against the formation of micelles (due to the large electrostatic repulsions between the components of the micelle) and against the formation of the surface layer (due to the strong stretching of the chains and the electrostatic repulsions). It is not clear whether the measured critical micellar concentration is the equilibrium one and whether the grafting density can reach equilibrium within the experimental time scale. This could reduce the adsorbed amount of copolymer to a lower value than predicted here with the thermodynamic equilibrium theory.

We also have not considered the effect of the ionic strength of the solution; even in pure water the ionic strength can be larger than the counterion concentration at the cmc. As long as the concentration of external salt is not larger than the concentration of counterions trapped in the brush, our results can be used but the concentration ρ must be replaced by the total free ion concentration which is much larger. The small concentration regimes predicted by eqs 21 and 22 are then unobservable, and the plateau in the adsorption isotherm is directly obtained at the cmc. At higher ionic strength screening becomes important both in the bulk and in the adsorbed layer and a more detailed theory is needed.

Finally, we have used the simplest possible model to describe the polyelectrolyte sequence, ignoring any excluded volume interaction and considering that the charged block of the copolymer is long enough ($N_A > N_B^{2/3}$). Most polyelectrolytes are in fact in a poor solvent, and a more refined theory should take the solvent quality into account.[23,24] This could modify quantitatively our results, in particular if the charge fraction is small. The case of shorter polyelectrolyte blocks is also of interest since it is closer to the behavior of simple anionic surfactants. The Manning condensation of the counterions on the micelles which has been ignored here must be considered in this limit.

Appendix: Image Charges

At the interface between oil and water or a solid and water, the dielectric constant is discontinuous; this discontinuity must be taken into account in the electrostatic calculations. This is easily done by introducing image charges. In this Appendix, we discuss the role of the image charges in the limit where the dielectric constant of the medium in contact with water is much lower than the dielectric constant of water (this is the case for oil or for a dielectric solid). The image charge of a point charge e has the same value e and is located at the symmetric position with respect to the interface.

As the copolymer solution is neutral, the total image charge vanishes. If there is no charge heterogeneity parallel to the interface, i.e. if the charge density in the solution varies only in the direction perpendicular to the interface, because of Gauss theorem, the image charges do not create any electric field in the solution. Image charges thus play an important role only if the charge density varies in the direction parallel to the interface.

In order to give a more quantitative estimate of this effect, we model the grafted polyelectrolyte layer at the interface as a collection of cylinders of length L and diameter b perpendicular to the interface with a uniform density of counterions. L is the size of the grafted layer, and if the polyelectrolyte is described by a blob model, b is of the order of the size of the blobs. The average distance between chains is $D = \sigma^{-1/2}$. Taking into account the image charge, we must thus calculate the electric field created by cylinders of length $2L$ symmetric with respect to the surface.

In the limit where there is actually a polymer brush, $D \ll L$ and the electric field can be approximately by that of infinite cylinders. The electric field lies then parallel to the interface. This way we only ignore the effect of the small region of size D at the edge of the layer where this is not true. Around each cylinder, there is a surface where the electric field vanishes; on average, it is a cylinder of size D. We calculate the electrostatic energy of one chain in a cylindrical cell of radius D by imposing that the electric field vanishes on the boundary of the cell. We obtain the electrostatic energy per chain due to the charge heterogeneity as

$$E_{el} = kTl_B(N_Af)^2/L\{\log v - {}^3/_4 + v^{-2} - {}^1/_4 v^{-4}\} \quad \text{(A-1)}$$

where $v = D/b$.

In the limit where $D = b$ the charge density is uniform and $E_{el} = 0$. The grafted polymer layer actually forms a brush if $D \ll L$; one can then explicity check that this *electrostatic energy is smaller than the translational* entropy of the counterions and can thus be neglected.

If the adsorbed layer does not form a brush but is very dilute ($D \gg L$), each chain only interacts with its own image. The extra electrostatic energy of each chain due to its adsorption is

$$E_{el} = kTl_B(N_Af)^2/L \log 2 \sim kTN_Af^{4/3}(l_B/a)^{2/3} \qquad \text{(A-2)}$$

This energy is much larger than kT and in the early stages of the adsorption where the polyelectrolyte brush has not yet formed, this electrostatic repulsion can constitute a large potential barrier against adsorption and slow down considerably the adsorption kinetics.

Finally, let us also notice that for dilute grafted polyelectrolyte layers, the image charge of a chain also controls its radius parallel to the interface. If in a first approximation we model the chain as a cylinder of length L making an angle θ with the normal to interface, the electrostatic energy is $E(\theta) = E_{el}(1 - \cos \theta)$. The equipartition of energy gives then the amplitude of fluctuation of the angle around the perpendicular to the interface

$$\theta = N_A^{1/2}f^{-2/3}(l_B/a)^{-1/3} \qquad \text{(A-3)}$$

The radius of the chain parallel to the interface is then

$$R_\parallel = N_A^{1/2}a \qquad \text{(A-4)}$$

This estimation neglects the lateral fluctuations of the chain around the rodlike configuration but these are of the same order of magnitude as $R_\parallel$ given by eq A-4. Notice that when the grafted chains form a brush, the parallel radius is also given by (A-4) and thus the parallel radius does not depend on the grafting density.

Acknowledgment. We acknowledge useful discussion with M. Banderet (Strasbourg), M. Tirrell (Minneapolis), and P. Pincus (Santa Barbara).

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