To evaluate the magnitude of the interfacial energy change in the presence of small solvents, we model the interface as a region where the A chain profile decays from its concentration in the corona, ϕ_0, to a surface density $\sigma = p(R_B/a)/4\pi$ at a point one segment length from the interface at $r = a$. Continuing with the mean-field model, we write the A chain concentration profile as[19]

$$\phi_A(r) = \sigma(r/a) \tag{A.1}$$

and the interfacial thickness as

$$d_I/a = \phi_0(36\pi N_B/p)^{1/3} \tag{A.2}$$

The Flory–Huggins mixing energy per chain in this region is then

$$\frac{f_{m,i}}{kT} = \frac{2\pi\phi_0 \ln (\phi_0/2)}{3pN_S}\left[\left(\left(\frac{3N_Bp}{4\pi}\right)^{1/3} + \phi_0\left(\frac{36\pi N_B{}^2}{p}\right)^{1/3}\right)^3 - \frac{3N_Bp}{4\pi}\right] \tag{A.3}$$

Evaluating this contribution to the micelle free energy shows that its magnitude is small, e.g., for $\chi_{BS}N_B = 16.73$, $f_{m,i}/kT = -0.57$, while the total micelle energy is $f/kT = -38.6$. Only at very small values of $\chi_{BS}N_B$ does the interfacial energy contribution grow to 10% of the total. In this limit of nearly soluble B blocks, the interface becomes more diffuse and a more detailed approach is warranted.

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Block Copolymers at Interfaces. 2. Surface Adsorption

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ABSTRACT: We present a theory for adsorption of diblock copolymers onto surfaces. We find that a critical adsorption concentration exists, analogous to the critical micelle concentration in micellization. This critical adsorption concentration decreases as the surface attraction increases, as the copolymer–solvent compatibility decreases, as the more soluble A block length decreases, and as the size of the solvent increases. The thickness of the adsorbed layer increases as the length of the A block increases, as the surface attraction for the anchoring B block increases, and as the solvent becomes smaller. We present a number of useful scaling relationships for layer thicknesses and surface densities as functions of block lengths of both the copolymer and the solvent. We are able to predict regions where only adsorption or only micellization are expected to occur.

I. Introduction

The behavior of amphiphilic diblock copolymers at interfaces plays an important role in the stabilization of colloidal particles in inks, paints, coatings, pharmaceuticals, and magnetic storage materials.[1] Stabilization of colloidal particles is realized by adsorption of diblock copolymers onto their surfaces. The block interacting unfavorably with the solvent adsorbs onto the surface of a particle while the solvated block extends into the solution and forms a steric layer thus imparting stability. This adsorption process is complicated by the tendency of amphiphilic block copolymers to form micelles if the concentration of the solution exceeds the critical micelle concentration. In the previous paper we investigated this micellization process in diblock copolymers as a function of the relative lengths of the blocks, the size of the solvent, and the solubility of the head group.[2] Here we extend the analysis to block copolymer adsorption.

Several reviews and monographs discuss homopolymer adsorption.[3-6] In general, homopolymers adsorb at several points along the chain in conformations having loops, trains, and tails.[7] Due to their amphiphilic nature, block copolymers adsorb in a very different fashion. Experiments have shown that diblock copolymers adsorb with one compact, tightly bound block and one extended, swollen block stretching away from the surface,[8] prompting researchers to model them as terminally anchored homopolymers. Previous investigators have studied the conformations of polymer layers where the polymers are attached to a surface by one end at a fixed surface density.[9,10] In this study, we allow the chains to reach the surface density and conformation determined by equilibration with the solution of block copolymers.

This paper concentrates on adsorption of block copolymers with small insoluble anchoring blocks in solutions of small solvent molecules. One motivation for focusing our attention on these systems arises from the observation that colloidal stability is improved by maximizing the number of chains on the surface.[1] We expect the surface density of adsorbed block copolymers to increase with

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decreasing anchoring unit size, hence we focus our attention on systems with small insoluble blocks. The molecular size of the solvent has an important effect on the free energy of mixing of a polymer molecule. Since most systems of practical importance contain a small solvent relative to the copolymer molecules, we investigate the effect of solvent size in this small solvent regime.

We first present a model employing a mean-field theory to describe block copolymer adsorption onto an excess adsorbing surface. This situation is often the case in colloidal dispersions where the available surface area is great. We introduce the idea of the critical adsorption concentration, cac, the concentration below which virtually no adsorption occurs and above which all additional copolymer to the system adsorbs onto the surface. We then describe the results of numerical calculations demonstrating that the critical adsorption concentration decreases as the surface attraction increases, as the copolymer–solvent compatibility decreases, as the more soluble A block length decreases, and as the size of the solvent increases. We also present some scaling relationships for the layer thickness and surface density of the adsorbed steric layer as functions of copolymer block length and solvent size. Finally we show regimes where micellization is preferred over adsorption and demonstrate that surface attractions of only a few kT are necessary to realize adsorption but that this requirement depends strongly on the nature of the polymer–solvent interactions.

II. Adsorption Model

As in ref 2 we consider a system of diblock copolymer chains having N_A segments of species A linked to N_B segments of species B immersed in a solvent S of N_s segments. Again we assume that the segment length of all species is a, and the total volume of our system is Ωa^3. We again study the effects of solvent size and block length by varying the parameters $\beta = N/N_s$, with $N = N_A + N_B$ and $\alpha = N_B/N_A$.

We adapt the lamellar micelle model of our previous paper[2] to describe adsorption by adding a surface–B segment interaction. The adsorbing diblock copolymers are assumed to form a planar layer along the surface consisting of a melt of B chains of thickness L_B located near the surface and an outer layer of A chains and solvent of thickness L_A and A-chain volume fraction ϕ_A as shown in Figure 1. The total layer thickness L_T is given by $L_T = L_A + L_B$. We introduce a dimensionless surface density, σ, such that the surface area per chain is a^2/σ.[9,11] As before, Flory's dimensionless interaction parameter χ_{BS} describes the interactions between B and S segments. Again, for simplicity, we consider athermal A–S interactions, i.e., $\chi_{AS} = 0$. Since $\chi_{AS} = 0$, $\chi_{BS}N_B$ represents the total effective interaction per chain and is a measure of the degree of incompatibility between the copolymer chains and the solvent for a fixed A chain length. We represent the surface–B monomer interaction by a dimensionless surface energy γ.

First we write the energy per chain of the adsorbed surface layer as

$$f_{\mathrm{ads}} = f_{\mathrm{def}} + f_{\mathrm{mix}} + f_{\mathrm{int}} + f_{\mathrm{surf}} \tag{1}$$

The first term is the elastic deformation energy of the copolymer chains in the layer[2,12–15]

$$f_{\mathrm{def}} = \tfrac{3}{2}kT\left(\frac{L_A^2}{N_A a^2} + \frac{N_A a^2}{L_A^2} + \frac{L_B^2}{N_B a^2} + \frac{N_B a^2}{L_B^2} - 4\right) \tag{2}$$

where k is the Boltzmann constant and T is the temperature.

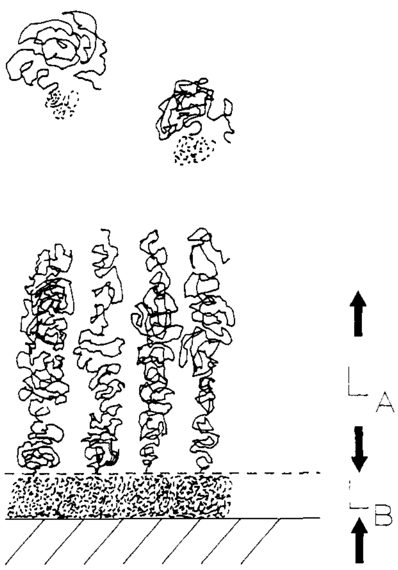

Figure 1. Schematic of the adsorption system. The adsorbed layer consists of a melt of B chains of thickness L_B at a surface density σ and an outer layer of thickness L_A consisting of solvent and A chains at volume fraction ϕ_A. The region outside the layer contains isolated A–B diblock copolymers and solvent molecules S.

The next contribution arises from the energy of mixing solvent molecules with the A chains in the outer layer given by

$$f_{\mathrm{mix}} = kT\left[\frac{\beta}{1+\alpha}\,\frac{1-\phi_A}{\phi_A}\ln(1-\phi_A) + \chi_{AS}N_A(1-\phi_A)\right] \tag{3}$$

where $\chi_{AS} = 0$ for this study. The interfacial energy per chain, f_{int}, is given by[16]

$$f_{\mathrm{int}} = \frac{kT}{\sigma}(\chi_{BS}/6)^{1/2} \tag{4}$$

The surface energy term, f_{surf}, is of a similar form

$$f_{\mathrm{surf}} = \frac{kT}{\sigma}\gamma \tag{5}$$

where γ is negative for an attractive surface–B monomer interaction and positive for a repulsive surface–B monomer interaction.[17]

The lengths L_A and L_B are related to the independent variables σ and ϕ_A by the incompressibility conditions

$$L_A = \frac{N\sigma a}{(1+\alpha)\phi_A} \tag{6}$$

and

$$L_B = \frac{\alpha N\sigma a}{1+\alpha} \tag{7}$$

Substituting for L_A and L_B and summing all the contributions gives the total energy per chain of the adsorbed layer as

$$\frac{f_{\mathrm{ads}}}{kT} = \tfrac{3}{2}\left(\sigma^2\alpha N_A + \frac{1}{\sigma^2\alpha N_A} + \frac{N_A\sigma^2}{\phi_A^2} + \frac{\phi_A^2}{N_A\sigma^2}\right) - 6 + \frac{\beta}{1+\alpha}\,\frac{1-\phi_A}{\phi_A}\ln(1-\phi_A) + \chi_{AS}N_A(1-\phi_A) + \frac{1}{\sigma}[(\chi_{BS}/6)^{1/2} + \gamma] \tag{8}$$

As with spherical micelles, it is important to remember that only a fraction, ζ, of the chains exists in the steric layer. The remainder of the chains reside in the bulk, and we consider the simplest case (and present arguments in section III.E supporting its validity) where only single, free chains are in equilibrium with the steric layer. The total energy of the system then comprises the energy of the adsorbed layer plus the energy of the solution outside the layer, F_{mix}, as

$$F_{\text{T}} = \Omega kT\left[\frac{\phi\zeta}{N}\frac{f_{\text{ads}}}{kT} + \frac{F_{\text{mix}}}{\Omega kT}\right] \tag{9}$$

where $\Omega\phi\zeta/N$ is the number of chains adsorbed. F_{mix} is given by

$$\frac{F_{\text{mix}}}{kT} = \frac{\Omega(1-\phi_{\text{L}})}{N_{\text{A}}(1+\alpha)}\left[\phi_{\text{sup}} \ln \phi_{\text{sup}} + \beta(1-\phi_{\text{sup}}) \times \ln(1-\phi_{\text{sup}}) + \chi_{\text{BS}}\alpha N_{\text{A}}\phi_{\text{sup}}\left(1 - \frac{\alpha\phi_{\text{sup}}}{1+\alpha}\right)\right] \tag{10}$$

where ϕ_{sup} is the volume fraction of copolymers in the supernatant outside of the layer and ϕ_{L} is the volume fraction of the layer. The relations for ϕ_{sup} and ϕ_{L} are

$$\phi_{\text{sup}} = \frac{\phi(1-\zeta)}{(1-\phi_{\text{L}})}$$

and

$$\phi_{\text{L}} = \phi\zeta\xi$$

where

$$\xi = \frac{1+\alpha\phi_{\text{A}}}{(1+\alpha)\phi_{\text{A}}}$$

The equilibrium values of σ, ϕ_{A}, and ϕ_{sup} are found by minimization of F_{T} with respect to these variables.

Minimization of F_{T} with respect to σ yields an explicit expression for σ in terms of ϕ_{A}, given in the Appendix, thus simplifying the problem to a minimization in two variables, ϕ_{A} and ϕ_{sup}.

III. Results and Discussion

In the following sections we describe the results of calculations of critical adsorption concentration, surface density, and layer thickness, investigating the effects of surface attraction, copolymer incompatibility, block length, and solvent size. Throughout most of the discussion we choose the A and B block lengths such that $\alpha = N_{\text{B}}/N_{\text{A}}$ is 0.1 and the total degree of polymerization $N = N_{\text{A}} + N_{\text{B}}$ is 200. In section D we study the adsorption dependence on N_{A}, N_{B}, and N_{S} individually. In section E we present regions where the formation of spherical micelles is favored over copolymer adsorption.

A. Critical Adsorption Concentration. At very low concentrations we expect the copolymer chains to exist as a random phase of isolated, free chains as found in studies of micellization. Similar to micellization, we expect that a concentration exists where these copolymers, having an affinity for the surface, will aggregate on the surface. In this case we define a critical adsorption concentration, cac, as the concentration below which virtually no copolymers adsorb onto the surface and above which nearly all additional copolymer adsorbs as demonstrated in Figure 2. Here the supernatant copolymer concentration is plotted as a function of the overall copolymer concentration for various degrees of incompatibility, $\chi_{\text{BS}}N_{\text{B}}$. In Figure 2, the supernatant concentration equals the overall copolymer concentration below the cac and becomes almost constant above the cac. We define the cac as the point where extrapolations from the two linear regimes intersect. Above the cac, the critical adsorption concentration represents the background supernatant concentration of free copolymer chains in equilibrium with the adsorbed layer. The critical concentration for adsorption decreases as B blocks become less compatible with the solvent or $\chi_{\text{BS}}N_{\text{B}}$ is raised as discussed in section III.C.

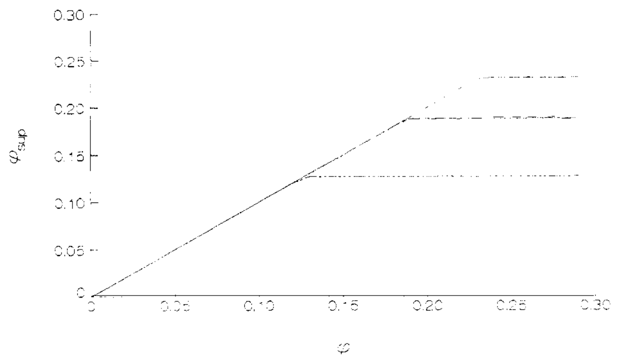

Figure 2. Free copolymer concentration as a function of the overall copolymer concentration for different degrees of incompatibility: $\chi_{\text{BS}}N_{\text{B}} = 9.1$ (—), 10.9 (- - -), 12.7 (···), 13.9 (– – – –) with $\alpha = N_{\text{B}}/N_{\text{A}} = 0.1$, 1, $\beta = N/N_{\text{S}} = 50$, $N = 200$, and $\gamma = -2$.

Table I
Supernatant Copolymer Concentration and Layer Thickness Relative to the Random Coil Dimension as a Function of the Surface Attraction for Different Copolymer–Solvent Compatibilities

	$\chi_{\text{BS}}N_{\text{B}}$					
	12.73		14.55		16.36	
$-\gamma$	ϕ_{sup}	$L_{\text{A}}/N_{\text{A}}^{1/2}a$	ϕ_{sup}	$L_{\text{A}}/N_{\text{A}}^{1/2}a$	ϕ_{sup}	$L_{\text{A}}/N_{\text{A}}^{1/2}a$
1.6	spherical	micelles	spherical	micelles	spherical	micelles
1.8	0.1825	3.10	spherical	micelles	spherical	micelles
2.0	0.1489	3.22	spherical	micelles	spherical	micelles
2.2	0.1182	3.3	spherical	micelles	spherical	micelles
2.4	0.0905	3.43	0.0597	3.44	spherical	micelles
2.6	0.0656	3.54	0.0386	3.54	spherical	micelles
2.8	0.0442	3.64	0.0218	3.64	spherical	micelles
3.0	0.0265	3.74	0.0102	3.73	0.0026	3.72
3.2	0.0135	3.84	0.0039	3.83	0.0008	3.82
3.4	0.0056	3.94	0.0013	3.93	0.0002	3.92
3.6	0.0019	4.03	0.0004	4.02	0.0001	4.01

B. Surface Attraction. The effect of the surface–B segment attraction is presented in Table I. Here the critical adsorption concentration and thickness of the A block layer are calculated as a function of $-\gamma$, the dimensionless surface energy, for various degrees of incompatibility. Values of $-\gamma$ range from 2.0 to 3.6, corresponding to an adsorption energy of a few kT per B segment, typical of values assigned to surface–segment attractions.[7] These values of $-\gamma$ correspond to dimensional surface tension values, $-\gamma kT/a^2$, of 16.8–30.2 dyn/cm at 300 K, similar to those reported for solid–liquid interfaces.[18,19]

In Table I we note that the surface layer thickness relative to the random coil dimension for A chains increases steadily as the surface attraction increases but can be nearly constant or decrease slowly as the B chain solvent compatibility drops. We can explain these trends by examining the approximation for ϕ_{sup} in the limits of large A blocks, $N_{\text{A}} \gg N_{\text{B}}$, N_{S} and small values of ϕ_{sup} given by

$$\phi_{\text{sup}} \simeq \exp\left[\frac{f_{\text{ads}}}{kT} + \beta - \chi_{\text{BS}}N_{\text{B}}\right] \tag{11}$$

with

$$\frac{f_{\mathrm{ads}}}{kT} \simeq \frac{3}{2}\left(\frac{N_{\mathrm{A}}\sigma^2}{\phi_{\mathrm{A}}^2} + \frac{1}{\sigma^2 \alpha N_{\mathrm{A}}}\right) - 6 + \frac{\beta}{1+\alpha}\,\frac{1-\phi_{\mathrm{A}}}{\phi_{\mathrm{A}}}\ln(1-\phi_{\mathrm{A}}) + \frac{1}{\sigma}\left[\left(\frac{\chi_{\mathrm{BS}}}{6}\right)^{1/2} + \gamma\right] \qquad (12)$$

At fixed $\chi_{\mathrm{BS}}N_{\mathrm{B}}$, increasing the surface attraction, $-\gamma$, lowers the adsorption energy through the last term of eq 12, thus lowering the cac. The mixing energy of eq 12 then gives rise to a secondary effect. The volume fraction of A chains in the outer layer, ϕ_{A}, decreases as $-\gamma$ increases to equilibrate with the lower copolymer concentration in the bulk (represented by cac). Also the layer thickness relative to the random coil size $L_{\mathrm{A}}/N_{\mathrm{A}}\alpha^{1/2}a$ increases with $-\gamma$ for a given $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ due to this swelling of the A layer. We also note that spherical micelles will form if the surface attraction is not sufficient to permit adsorption as discussed in more detail below.

At a fixed value of the surface attraction, $-\gamma$, Table I shows that the supernatant concentration decreases as $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ increases in accord with eq 11 for all values of $-\gamma$. Two trends for the relative thickness, $L_{\mathrm{A}}/N_{\mathrm{A}}^{1/2}a$, as a function of $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ are evident in Table I. For lower values of $-\gamma$, $L_{\mathrm{A}}/N_{\mathrm{A}}^{1/2}a$ is constant or increases slightly as $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ increases as shown for $-\gamma = 2.4$–2.8. In this case the mixing energy term is dominant over the surface attraction term in eq 12, resulting in a slight swelling of the layer as it equilibrates with a lower supernatant copolymer concentration represented by cac.

For larger values of $-\gamma$, the surface attraction term of eq 12 dominates the mixing energy leading to a slight compression of the absorbed layer as $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ increases. As the copolymer molecules become less compatible with the solvent, they adsorb more compactly causing the surface density, σ, and the volume fraction, ϕ_{A}, to increase. The volume fraction, ϕ_{A}, increases more rapidly than σ causing $L_{\mathrm{A}}/N_{\mathrm{A}}^{1/2}a$ to decrease through eq 6.

C. Incompatibility. As mentioned in section II, we consider athermal interactions for the A chain, and thus $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ is a gauge of the incompatibility of the system for a fixed A block length.[2,13,14] In Figure 3 we demonstrate how the cac varies with the degree of incompatibility for different values of $\beta = N/N_{\mathrm{S}}$ for a fixed surface energy of $-\gamma = 2$. As the copolymer chains become less compatible with the solvent, the concentration required to form an adsorbed layer declines until a degree of incompatibility is reached where spherical micellization is favored over adsorption. The point where the transition from adsorption to micellization occurs is found by comparing the free energy of a chain in the adsorbed layer to that of a chain in a micelle. We also note from Figure 3 that as the solvent size becomes smaller, the cac increases for a given degree of incompatibility and the point where micellization is favored over adsorption occurs at a higher critical concentration and lower compatibility.

When the surface attraction is small compared to the mixing energy as in this case, ϕ_{A} decreases slightly to equilibrate with the decreasing supernatant concentration as $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ increases as discussed in section III.B. To realize this slight swelling in the A layer, L_{A} increases slightly and σ decreases slightly as $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ increases. However, despite the large effect of $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ on the cac, ϕ_{A}, σ, and L_{A} are only weakly dependent on $\chi_{\mathrm{BS}}N_{\mathrm{B}}$ due to the geometric constraints of the layer. The typical values, $L_{\mathrm{A}}/N_{\mathrm{A}}^{1/2}a$ and σ, are about 3.25 and 0.1, respectively.

D. Block Length and Solvent Size. We show the layer thickness L_{A} as a function of the length of the A block, N_{A}, for various B block lengths in Figure 4a. The B block lengths are small compared to the A block lengths; thus the A layer thickness, $L_{\mathrm{A}} = L_{\mathrm{T}} - L_{\mathrm{B}}$, is only slightly less than the total layer thickness. Figure 4a demonstrates that the A layer thickness increases with N_{A} but not linearly as predicted for a fixed surface density by scaling theories[8,9,11] (and eq 6 of this theory).[20] Instead we find that as N_{A} increases the copolymer chains occupy a larger surface area; hence the surface density decreases as shown in Figure 4b. The scaling laws for σ and L_{A} with N_{A} are $\sigma \sim N_{\mathrm{A}}^{-0.3}$ and $L_{\mathrm{A}} \sim N_{\mathrm{A}}^{0.7}$ for all B block lengths in Figure 4.

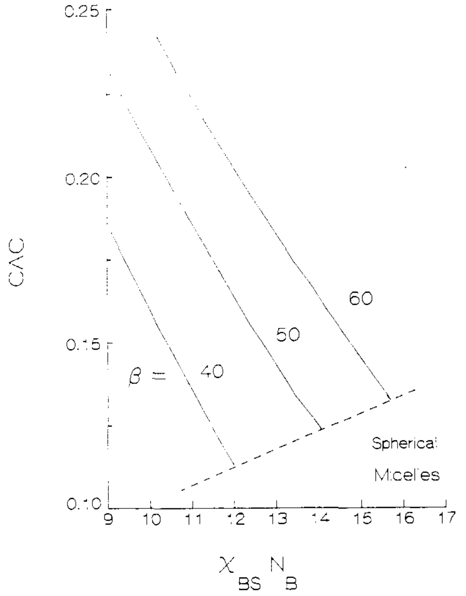

Figure 3. Critical adsorption concentration as a function of the solvent–B chain interaction, $\chi_{\mathrm{BS}}N_{\mathrm{B}}$, for the same conditions as in Figure 2.

The results of Figure 4 apply to conditions where the B block is much smaller than the A block and the surface attraction is high enough to ensure that adsorption occurs rather than micellization. In this limit the critical adsorption concentration is given by

$$\mathrm{cac} \simeq \exp\left[\frac{f_{\mathrm{ads}}}{kT} + \beta\right] \qquad (13)$$

with

$$\frac{f_{\mathrm{ads}}}{kT} \simeq \frac{3}{\phi_{\mathrm{A}}}\left(\frac{N_{\mathrm{A}}}{N_{\mathrm{B}}}\right)^{1/2} + \frac{\beta}{1+\alpha}\,\frac{1-\phi_{\mathrm{A}}}{\phi_{\mathrm{A}}}\ln(1-\phi_{\mathrm{A}}) + \frac{\gamma(N_{\mathrm{B}}N_{\mathrm{A}})^{1/4}}{\phi_{\mathrm{A}}^{1/2}} \qquad (14)$$

where a limiting expression for the surface density

$$\sigma \simeq \left[\frac{\phi_{\mathrm{A}}}{(N_{\mathrm{B}}N_{\mathrm{A}})^{1/2}}\right]^{1/2} \qquad (15)$$

has been applied.

A number of things occurring when N_{A} is increased can be explained by these equations. First, since ϕ_{A} increases only slowly with N_{A}, we see from eq 6 and 15 that L_{A} increases with N_{A} as expected, but the dimensionless surface density, σ, decreases with N_{A}. We also note that the degree of stretching, represented by $L_{\mathrm{A}}/N_{\mathrm{A}}^{1/2}a$, increases with N_{A}.

The critical adsorption concentration increases with N_{A} since the dominant term of eq 13, $\beta = N/N_{\mathrm{S}}$, increases linearly with N_{A}. To balance the increase in mixing energy of the free chains represented by β in eq 13, the concen-

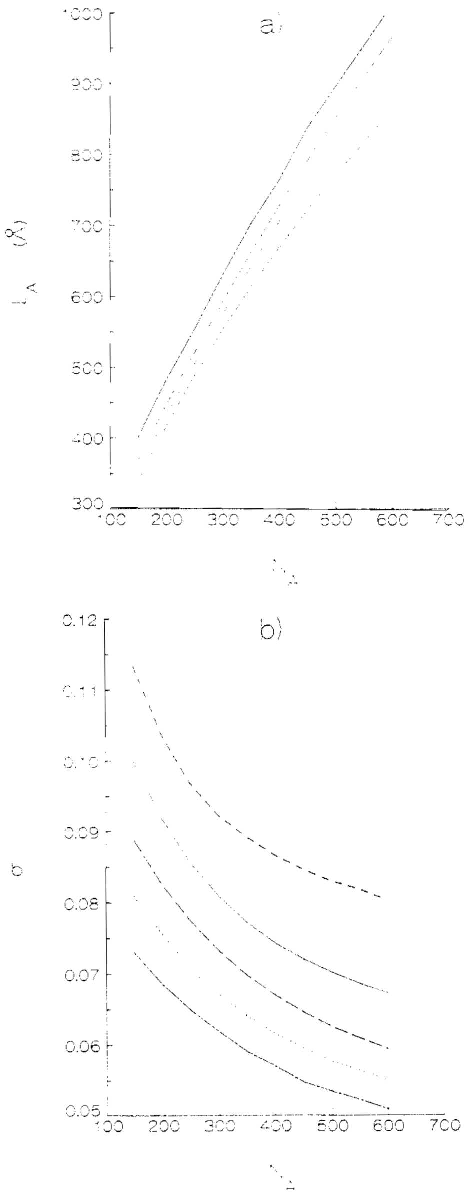

Figure 4. (a) Layer thickness L_A as a function of N_A, assuming a monomer size $a = 7$ Å. (b) Surface density σ as a function of N_A. The conditions are $N_S = 4$, $\chi_{BS} = 0.7$, $\gamma = -4$, and $N_B = 15$ (- - -), 20 —, 25 (– –), 30 (···), and 35 (– - –).

tration of the A chains in the adsorbed layer, ϕ_A, increases slightly, increasing the energy of mixing in the layer represented by the second term of eqn. (14). Therefore increasing the length of the A block increases the thickness L_A and decreases the surface density σ as expected but also causes the volume fraction ϕ_A to increase.

Figure 4a,b also demonstrates the effect of the anchoring B block length on the layer thickness and surface density. Increasing the B block length causes the cac to occur at a lower concentration for a fixed A block length due to the diminished compatibility, $\chi_{BS}N_B$, as discussed earlier. Thus, for larger B blocks, a more dilute supernatant phase is in equilibrium with the adsorbed layer than for smaller B blocks. The A chains equilibrate with the dilute bulk phase by swelling, increasing L_A and decreasing ϕ_A. The scaling dependence of L_A on N_B is $L_A \sim N_B^{0.17}$. Furthermore, the surface density decreases as the anchoring B block length increases, as expected following the relationship $\sigma \sim N_B^{-0.5}$.

The solvent size also affects the cac, layer thickness, and surface density. Figure 5a shows how the cac varies with N_S for a fixed degree of polymerization, $N = N_A + N_B$. As

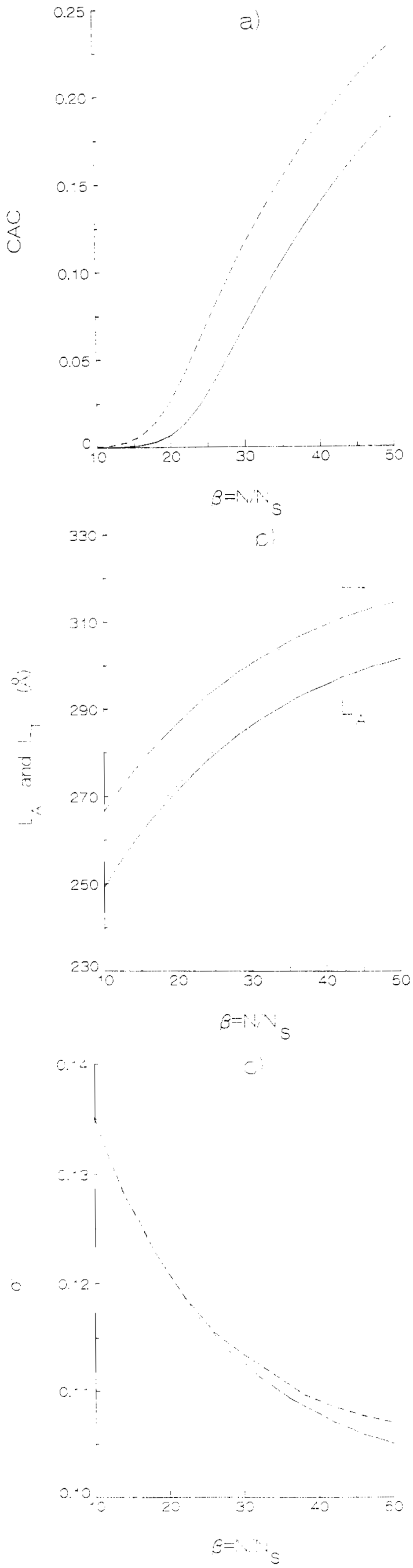

Figure 5. (a) Critical adsorption concentration versus $\beta = N/N_S$ for $\chi_{BS}N_B = 9.1$ (- - -) and 10.9 (—). (b) Total layer thickness L_T and A layer thickness L_A for $\chi_{BS}N_B = 9.1$ (···) and 10.9 (—) as a function of $\beta = N/N_S$. (c) Surface density as a function of $\beta = N/N_S$ for $\chi_{BS}N_B = 9.1$ (- - -) and 10.9 (—). Here $\alpha = N_B/N_A = 0.1$, $N = 200$, and $\gamma = -2$.

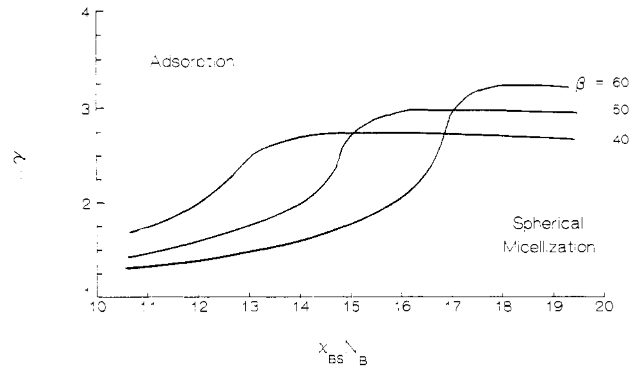

Figure 6. Adsorption and spherical micellization regions for $\chi_{BS}N_B$ and $-\gamma$. Here $\beta = N/N_S$ = 40, 50, and 60; $\alpha = N_B/N_A$ = 0.1; and N = 200.

the size of the solvent decreases, the enhanced mixing with free copolymer chains requires higher concentrations to achieve adsorption. Also, decreasing the solvent size swells the layer causing L_A, and therefore L_T, to increase and σ to decrease as shown in parts b and c of Figure 5, respectively. The layer thickness and surface density have a less pronounced dependence on the solvent chain length than on the copolymer block lengths; their relationships are $L_A \sim N_S^{-0.1}$ and $\sigma \sim N_S^{0.16}$.

Again we see that the surface density and layer thicknesses are relatively insensitive to χ_{BS}.

E. Adsorption–Micellization Regimes. In Figure 6 we show regions where we expect adsorption and spherical micellization to occur provided that the overall copolymer concentration is above the cac and the cmc, respectively. In the adsorption region, the lower free energy of the adsorbed layer precludes the formation of spherical micelles, thus forming an adsorbed layer below the critical micelle concentration. Of course, when the overall concentration is below the cac in this region, we have neither adsorption nor micellization. Similarly, in the region of spherical micellization, the free energy of micellization is lower than that for adsorption, preventing the formation of an adsorbed layer. The line separating the two regions designates the line where the free energy of micelles equals that of adsorbed layers and the cac equals the cmc.

Figure 6 demonstrates that for a given degree of incompatibility, $\chi_{BS}N_B$, increasing the surface attraction favors adsorption. More interestingly, we see that for $-\gamma$ of a few kT, we can move from a region of adsorption to spherical micellization simply by decreasing the compatibility of the system. However, it does appear that adsorption will occur for all $\chi_{BS}N_B$ if $-\gamma$ exceeds a certain value.

In the region of low compatibility, to the right of Figure 6, the values of the cac and the cmc are small and consequently ϕ_A is low. In this region the mixing energy of both the A chains in the layer and the free copolymer chains outside the layer dominate the surface attraction energy, thus requiring higher surface attractions for adsorption in this region. More specifically, in this region of high $\chi_{BS}N_B$ where mixing energies are important, smaller solvents, i.e., β = 60, further enhance mixing thus necessitating higher attractions for adsorption.

To the left side of Figure 6, where $\chi_{BS}N_B$ is smaller, the values for the cac and the cmc are moderate, rendering the mixing energies less important than above. Here the surface energy driving the adsorption dominates, requiring smaller attractions to overcome the mixing energies and adsorb. For smaller solvents, ϕ_A is lower due to the same swelling effects mentioned above and thus the A layer is less compact. In this case the surface density σ is smaller, and therefore $1/\sigma$ of the last term in eq 12, representing the number of B monomer–surface contacts, is larger. Since $1/\sigma$ is larger, smaller $-\gamma$ values are needed to realize adsorption for smaller solvents than for large solvents.

IV. Conclusions

In conclusion, we have presented results for the adsorption of diblock copolymers for various surface attractions, copolymer–solvent interactions, and a range of A–B block lengths and solvent sizes. We find that a critical adsorption concentration can be defined for situations of excess surface, in analogy with a critical micelle concentration for micellar systems. This critical adsorption concentration decreases as the surface attraction increases and as the copolymer–solvent incompatibility, $\chi_{BS}N_B$, increases. In fact, for a given surface attraction, the cac decreases as the incompatibility increases until a value of $\chi_{BS}N_B$ is realized where spherical micellization precludes adsorption. Furthermore, the thickness of the adsorbed layer increases as the surface attraction increases while $\chi_{BS}N_B$ has only a small effect. The adsorbed layer thickness increases as the A block length, N_A, increases according to the relationship $L_A \sim N_A^{0.7}$, and the surface density varies with N_A as $\sigma \sim N_A^{-0.3}$. Also the layer thickness increases as N_B increases due to swelling effects in the A layer. As expected the surface density decreases as the B block length increases, following the relation $\sigma \sim N_B^{-0.5}$. In addition to the effects of copolymer block lengths, decreasing the solvent size swells the outer A layer causing it to increase in thickness and decrease in surface density. We also demonstrate that with this model we can predict regions where only adsorption or only micellization are expected to occur.

Acknowledgment. This work was initiated with support from the Center for Materials Research at Stanford University under the NSF-MRL program. We gratefully acknowledge the support of the Procter & Gamble Corp. through their UERP program and the donors of the Petroleum Research Fund, administered by the American Chemical Society. M.R.M. was supported by an IBM Graduate Fellowship.

Appendix

Minimization of F_T with respect to σ yields the expression

$$\sigma^4 - \left[\frac{\left(\dfrac{\chi_{BS}}{6}\right)^{1/2} + \gamma}{3N_A\left(\alpha + \dfrac{1}{\phi_A{}^2}\right)}\right]\sigma - \frac{\left(\dfrac{1}{\alpha} + \phi_A{}^2\right)}{N_A{}^2\left(\alpha + \dfrac{1}{\phi_A{}^2}\right)} = 0 \qquad \text{(A1)}$$

which has the solution

$$\sigma = \frac{u_1{}^{1/2} + \left[u_1 - 4\left[\dfrac{u_1}{2} - \left(\left(\dfrac{u_1}{2}\right)^2 - b_0\right)^{1/2}\right]\right]^{1/2}}{2} \qquad \text{(A2)}$$

where

$$u_1 = [r + (q^3 + r^2)^{1/2}]^{1/3} + [r - (q^3 + r^2)^{1/2}]^{1/3}$$

$$q = \frac{4}{3}\,\frac{\left(\dfrac{1}{\alpha} + \phi_A{}^2\right)}{N_A{}^2\left(\alpha + \dfrac{1}{\phi_A{}^2}\right)}$$

$$r = \frac{1}{18}\frac{\left(\left(\frac{\chi_{\mathrm{BS}}}{6}\right)^{1/2} + \gamma\right)^2}{\left(N_{\mathrm{A}}\left(\alpha + \frac{1}{\phi_{\mathrm{A}}^2}\right)\right)^2}$$

and

$$b_0 = \frac{-\left(\frac{1}{\alpha} + \phi_{\mathrm{A}}^2\right)}{N_{\mathrm{A}}^2\left(\alpha + \frac{1}{\phi_{\mathrm{A}}^2}\right)}$$

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Surface Interactions in Compatible Polymer (and Block Copolymer) Solutions

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Received August 3, 1987

ABSTRACT: We study theoretically the effects of competing surface interactions in a system of two miscible polymers (A and B) in a good solvent, using the self-consistent mean-field formulation with ground-state dominance, as is appropriate to moderately concentrated systems. We take the A chains to be attracted to the surface and the B chains to be repelled. From susceptibility arguments, one expects a wide A-rich zone to appear at the surface, close enough to the A–B demixing transition. This (and several other qualitative expectations) is confirmed here by explicit numerical and analytic calculations of (1) concentration profiles and (2) interfacial energies, for various values of the excluded volume parameters and bulk concentrations. Our results are also applicable to the description of A–B block copolymer solutions with competing surface interactions.

1. Introduction

The physics of polymer–surface interactions and polymer adsorption phenomena has been of experimental and theoretical interest for a number of years.[1-11] Recently, particular attention has been paid to the surface properties of multicomponent polymer systems, especially to the structure and energetics of the interface between immiscible simple polymers and/or block copolymers in solutions and blends.[12-17]

In the present work, we extend the study of interfacial properties of multicomponent polymer systems in a somewhat different direction. Our concern is with the system polymer A + polymer B + good solvent (with A and B compatible) interacting with a boundary surface that is attractive to one polymer species (A) but repulsive to the other (B). This situation can presumably be realized experimentally, although we known of no example involving the mica surfaces that so far have ordinarily been used for this type of experiment.[10-11,14-15] We will presume the bulk concentrations of the two species to be high enough that mean-field theory is applicable and, moreover, that the surface interactions are of such a strength that the assumption of "ground-state dominance"[18] is appropriate for both polymer species. (For a comprehensive review of these ideas, see ref 4.)

As will become clear, under these conditions, much of the physics is controlled by the A–B excluded volume interaction, w_{AB}. For example, if this is zero, the A and B profiles are just those given in ref 3 for independent systems of attracted (A) and repelled (B) polymers. Whenever the coupling w_{AB} is nonzero, however, new effects arise, in both the interfacial energy and the concentration profiles of the two species. For example, when this coupling is strongly enough repulsive that the bulk A–B mixture is close to phase separation, the surface interaction can induce a strong local segregation, and the concentration profiles of A and B are extremely different from those that each polymer would have in the absence of the other.

While our discussion is phrased in terms of a mixed solution of A and B chains, it is notable that given our assumption of ground-state dominance, the computed profiles also apply (under appropriate conditions of con-

0024-9297/88/2221-1372$01.50/0