Diffusion of Copolymer Surfactant to a Polymer/Polymer Interface

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ABSTRACT: I consider a situation in which a homogeneous concentration of diblock copolymer greater than the critical micelle concentration (cmc) is initially added to phase I of a system of two immiscible polymer liquids (I and II), and diffuses to the interface. I consider only diffusion-limited transport, in which micelle dissolution and interfacial adsorption and desorption "reactions" are assumed to be rapid, while allowing for both free molecule and micelle diffusion. In an early time regime during which surfactant accumulates on the interface, an "exclusion zone" with no micelles is created near the interface. If the surfactant has a non-negligible solubility in phase II, there also exists an intermediate time regime during which copolymer diffuses through the interface without further interfacial accumulation, leading to a time-independent interfacial coverage and interfacial tension while transport continues. The exclusion zone may either close at intermediate times, which leads to an interfacial tension equal to the equilibrium value for a micellar solution, or it may persist, leading to a higher nonequilibrium tension, depending on the rate of diffusion into phase II. Asymptotically exact solutions to the diffusion problem are given for both early and intermediate times, in which the width of the exclusion zone (when present) increases with time t as $\sqrt{t}$.

1. Introduction

When a diblock copolymer is added to a system of two immiscible homopolymer melts as a surfactant, its effectiveness depends upon how much copolymer actually adsorbs to an interface. Because of the slow diffusion of both dissolved copolymer molecules and of copolymer micelles in a polymeric matrix, the amount of interfacial adsorption is often controlled by diffusion rather than by equilibrium thermodynamics. Limitations on the transport of copolymer to the interface can be important both in mechanically mixed blends, in which block copolymer is added to aid dispersion, and in experiments that measure the effect of added block copolymer upon the interfacial tension between immiscible homopolymers.

Throughout this paper, I consider a situation in which copolymer is initially added to one of two immiscible phases (phase I), and then begins to diffuse to the interface and into the other (phase II). I assume throughout that transport is entirely diffusion limited, and that micelle dissolution "reactions" and the adsorption and desorption of polymers from the interface are rapid. In this limit, the first stage of the transport process is diffusion-limited accumulation of copolymer at the interface. This process has been discussed previously by Semenov[1] for systems in which the initial copolymer concentration is below the critical micelle concentration (cmc) of phase I, so that no micelles are formed, and for which the copolymer is completely insoluble in phase II. The related problem of reactive coupling of end-functionalized polymers at an interface has also been considered by two different groups.[2−4] In this paper, I consider how the interfacial accumulation of premade block copolymer surfactants is modified by the presence of micelles in phase I, and at somewhat later times, by a non-negligible solubility of copolymer in phase II.

When micelles are present in phase I, diffusion can occur by diffusion of both dissolved free molecules and of micelles. It is found, however, that, in the limit of interest, free-molecule and micellar diffusion occur in different regions of space. If the destruction and creation of micelles, and the exchange of copolymer between micelles and the surrounding matrix, occur sufficiently rapidly, then a concentration of free copolymer nearly equal to the cmc will be maintained anywhere the local copolymer concentration exceeds the cmc. Because this prevents the formation of a gradient in free molecule concentration, it prevents the creation of any net flux of copolymer by free molecule diffusion in any region that contains micelles. During the early stages of accumulation of copolymer along an initially bare interface, the copolymer concentration will be suppressed below the cmc near the interface, if the interface is also assumed to be in diffusional equilibrium with its surrounding (i.e., if interfacial adsorption is rapid). In the diffusion-controlled limit of rapid micelle dissolution and interfacial adsorption, there must thus initially exist a region near the interface that is free of micelles. In this micelle "exclusion zone", transport can occur only by free molecule diffusion. Conversely, farther from the interface, where micelles do exist, transport can occur only by micellar diffusion.

The dynamics of interfacial accumulation can also be affected by solubility of the copolymer in phase II. If the solubility of free copolymer in phase II is not negligible compared to its solubility in phase I, then equilibrium is reached only when an equilibrium partitioning of surfactant between the two phases is established. The time required to repartition surfactant between phases when micelles are initially present in phase I is generally of order the time for the copolymer to diffuse over the entire volume of phase II. If phase II is macroscopic, this equilibration time can be much longer than the time required initially to accumulate a monolayer. When the solubility in phase II is not negligible, and the volume of phase II is large, it becomes convenient to distinguish between early, intermediate, and late time regimes. In the early time regime, an interfacial monolayer is created. During this period, most of the copolymer that diffuses to the interface during this period accumulates there. In the intermediate time regime, the rate of accumulation at the interface becomes negligible, but copolymer continues to diffuse through the interface from phase I into phase II. In the late (or equilibrium) time regime, the system reaches an equilibrium state in which the copolymer concentration is homogeneous

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throughout phase II. It is shown here that the chemical potential of copolymer at the interface, which controls the interfacial tension, generally becomes independent of time in the intermediate time regime, during which copolymer continues to be transferred between the phases.

This analysis was motivated by consideration of experiments that measure the effect of adsorbed copolymer upon polymer−polymer interfacial tension. Such experiments have been carried out both using pendent drop tensiometers[5−13] and, in experiments that directly motivated this analysis, using a spinning a spinning-drop tensiometer.[14] In both types of instrument, interfacial tension is inferred from the deformation of a drop of one liquid surrounded by a matrix of another. The deformation is caused by gravitational forces acting on a pendent drop or centrifugal forces acting on a spinning drop.

In such measurements, transport limitations arising from the repartitioning of copolymer between the matrix and drop can be severe if the copolymer has a comparable solubility in both phases. Consider an experiment in which a nearly symmetric diblock copolymer is initially added to the matrix phase in either type of tensiometer, and begins to diffuse into the drop. An equilibrium partitioning of copolymer between the matrix and drop can be obtained only by waiting for copolymer to diffuse a distance of order the drop radius, which is typically of order a millimeter. As an example, consider a copolymer with a diffusivity of $D = 5 \times 10^{-10}$ cm ^{2}/s, which is our estimate for a particular 10 kDa symmetric poly(isoprene-*b*-dimethylsiloxane) copolymer in a polyisoprene matrix.[14] Setting 1 mm $^2 = 2Dt$ yields a time $\tau_{eq} \sim 10^7$ s to diffuse to the center of the drop, or about 4 months. This time scale can be decreased by decreasing the drop diameter (as occurs naturally in a spinning drop tensiometer as the drop extends), but can also be much longer in systems of higher molecular weight polymers or polymers with higher glass transition temperatures. The time to diffuse to the center of a macroscopic drop often, however, remains longer than the time scale of such measurements. The observation that the system can exhibit an intermediate time regime in which the interfacial tension is independent of time is relevant to the interpretation of these experiments, since it implies that observation of a time independent interfacial tension does not necessarily indicate that equilibrium has been reached. This observation is most relevant to measurements on systems containing nearly symmetric A-*b*-B diblock copolymers, which are optimal surfactants for A/B blends from a purely equilibrium point of view, but also have comparable solubilities in A and B homopolymers.

2. Problem Statement

Consider the following problem: A diblock copolymer surfactant is initially mixed homogeneously throughout a matrix of the nearly pure homopolymer A (phase I), and begins to diffuse to the interface between the matrix and a drop of initially pure homopolymer B (phase II). In this paper, I focus on early and intermediate time regimes during which the distance over which the copolymer has time to diffuse in either phase is much less than the drop radius. The problem may be approximated over these time regimes as diffusion of a solute from one semi-infinite domain to an essentially flat interface and into another semi-infinite domain. I thus consider a simplified one-dimensional problem of diffusion to and through a flat interface at $z = 0$, where z is a coordinate measured perpendicular to the interface. Phase I is taken to occupy the half space $z > 0$, with an initial copolymer concentration c_0, while phase II occupies the space $z < 0$, with a vanishing initial concentration.

To discuss systems in which micelles may be formed, we must distinguish at each point a local concentration $c_f(z)$ of molecularly dissolved "free" copolymer and a local concentration $c_m(z)$ of copolymer in micelles, such that $c(z) = c_f(z) + c_m(z)$ is the total local copolymer concentration. A slightly simplified view of micellization is adopted, in which the concentration $c_f(z)$ of free molecules is assumed to be equal to the critical micelle concentration (cmc) in the phase of interest, denoted by c_c, at any point at for which $c(z) > c_c$. Let c_c^I and c_c^{II} be the critical micelle concentrations in phases I and II, respectively. This description assumes that the equilibrium between free copolymer and micelles can be adequately described by a simple limit of solubility (which is equivalent to neglecting the translational entropy of the micelles relative to that of the free molecules) and that the reactions by which micelles are created and dissolved are rapid enough to maintain local equilibrium between micelles and free copolymer at every point in the system.

Let Γ be the interfacial coverage of copolymer absorbed to the interface per unit area, and let $c_i^I \equiv c_f(0+)$ and $c_i^{II} = c_f(0-)$ be the concentrations of free copolymer infinitesimally close to the interface in phases I and II, respectively. We assume a local equilibrium relation $\Gamma = c_i^I L^I = c_i^{II} L^{II}$ in which L^I and L^{II} are partition coefficients with units of length. The dimensionless ratio $K \equiv L^{II}/L^I = c_i^I/c_i^{II}$ is a partition coefficient for free copolymer between the two bulk phases. The adsorbed layer on the interface is generally not dilute, so there need not exist an ideal linear relationship between interfacial coverage Γ and the activity of adsorbed polymer. We may account for any such nonideality by allowing L^I and L^{II} to be functions of Γ, rather than constants. The ratio $K = L^{II}/L^I$ is assumed to be constant, however, because the concentrations of dissolved free copolymer are assumed to remain very low.

Copolymer may be transported both by diffusion of free copolymer and by diffusion of micelles. Let D_f^I and D_f^{II} be the diffusion coefficients of free copolymer in phases I and II, respectively, and D_m^I and D_m^{II} be the micelle diffusivities in the corresponding phases. The assumption that $c_f(z)$ remains equal to the cmc throughout regions in which micelles are present has an important implication for transport: There can be no diffusive flux $J = D_f(dc_f(z)/dz)$ of free molecules in regions containing micelles, because there can be no gradient in the concentration $c_f(z) = c_c$ of free copolymer in such regions. Diffusion of copolymer must thus occur by micellar diffusion alone in regions with $c(z) > c_c$, in which micelles are present, and by diffusion of free molecules alone in regions with $c(z) < c_c$, where c_c is the cmc of the phase of interest.

The remainder of the paper is organized as follows: section 3 reviews the simpler case in which no micelles are formed in either phase. Sections 4 and 5 discuss the early and intermediate time regimes, respectively, for the case in which $c_0 > c_c^I$, so that micelles are initially formed in phase I, but in which micelles are never formed in phase II. Section 6 presents a similarity solution to the transport problem considered in sections 4 and 5 that provides an asymptotically exact description of both the earliest stage of interfacial accumulation and of the intermediate time regime, though not of the crossover between early and intermediate times. Section 7 discusses the intermediate and late stages of transport in a thermodynamically inverted situation in which micelles are initially formed in phase I, but in which the system evolves toward an equilibrium state in which micelles can eventually exist only in phase II. Section 8 is a summary of conclusions.

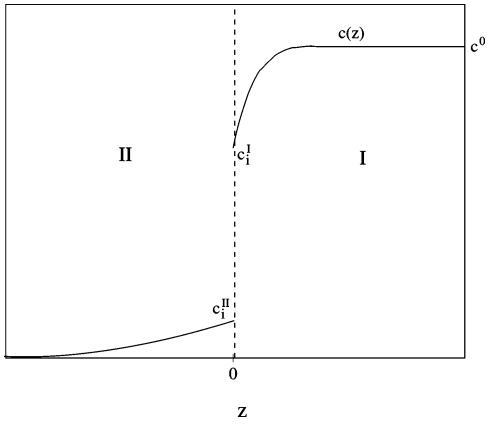

Figure 1. Schematic diagram of the concentration $c(z)$ of dissolved copolymer surfactant near an interface between phases I and II, when the concentration remains below the cmc in both phases. The concentrations c_i^I and c_i^{II} on either side of the interface are related by a partition coefficient $K = c_i^I/c_i^{II}$

3. Diffusion without Micelles

We begin by reviewing the simple case shown in Figure 1, in which the initial concentration c_0 is below the cmc (i.e., $c_0 < c_c^I$and $c_0/K < cc_i^I$), in which no micelles are formed in either phase.

3.1. Early Times: Interfacial Accumulation. First consider the initial growth of an adsorbed interfacial layer of copolymer at very small time t, immediately after the onset of diffusion. As long as $c_i^I(t) = \Gamma(t)/L^I$ remains much less than c_0, we may approximate $c(z,t)$ by the solution obtained with an absorbing boundary condition $c_i^I(t) \simeq 0$. This yields an asymptotic approximation for $c(z)$ at early times as an error function, $c(z) = c_0\mathrm{erf}(z/\sqrt{4D_f^I t})$, and a corresponding flux

$$J_I(t) \simeq c_0\sqrt{D_f^I/(\pi t)} \tag{1}$$

to the interface from phase I. In the absence of signficant flux into phase II, we may set $d\Gamma(t)/dt = J_I(t)$ and thereby obtain an interfacial coverage $\Gamma(t) \simeq 2J_I(t)t$ that initially grows as $\Gamma(t) \propto \sqrt{t}$.

If the flux into phase II remains negligible throughout the period in which Γ increases, Γ will increase as roughly $\sqrt{t}$ until it reaches a final value $\Gamma_0 = c_0L^I$ for which the interface is in equilibrium with the bulk concentration. This requires a time

$$\tau_{acc} \sim \frac{(L^I)^2}{D_f^I} \tag{2}$$

of order the time at which the initial $\sqrt{t}$ growth of $\Gamma(t)$ extrapolates to a value $\Gamma(\tau_{acc}) \simeq \Gamma_0$.

We next consider the flux into phase II during this initial accumulation, which has thus far been neglected. The flux $J_{II}(t) \simeq D_f^{II}(dc_f/dz)$ into phase II will be of order $J_{II}(t) \sim D_f^{II}(c_i^{II}/\sqrt{D_f^{II}t})$, where $\sqrt{D_f^{II}t}$ is roughly the distance over which the copolymer diffuses into phase II during time t. By setting $c_i^{II} \simeq \Gamma/L^{II}$ and $\Gamma(t) = 2J_I(t)t \propto \sqrt{t}$, we find a flux $J_{II}(t) \sim \sqrt{D_ID_{II}}c_0/L^{II}$ that is constant at early times. In contrast to this, $J_I(t)$ diverges as $1/\sqrt{t}$ as $t\rightarrow 0$. As a result, the ratio

$$J_{II}(t)/J_I(t) \sim \sqrt{D_f^{II}}t/L^{II} \tag{3}$$

is always negligible at sufficiently early times.

Equation 3 predicts that $J_{II}(t)$ will become comparable to $J_I(t)$ at a time

$$\tau_{leak} \sim (L^{II})^2/D_f^{II} \tag{4}$$

This prediction is valid only if $\Gamma(t)$ continues to increase as $\sqrt{t}$ until $t \sim \tau_{leak}$, which can only occur if $\tau_{leak} \ll \tau_{acc}$. If so, $\Gamma(t)$ will saturate at a time $t \sim \tau_{leak}$ at which $J_I \sim J_{II}$ to value significantly less than Γ_0. Alternatively, if eq 4 yields a time $\tau_{leak} \gg \tau_{acc}$, then $\Gamma(t)$ will saturate to a value very close to Γ_0 at a time $t \sim \tau_{acc}$, before leakage into phase II becomes significant. To quantify the signficance of copolymer diffusion into phase II, it is thus useful to introduce a dimensionless parameter

$$P \equiv \frac{D_f^{II}}{D_f^I}\frac{1}{K^2} \tag{5}$$

such that $P \propto \tau_{acc}/\tau_{leak}$. Flux into phase II will signficantly decrease the interfacial concentration at intermediate times if $P > 1$.

3.2. Intermediate Times: Transport Between Phases. During the intermediate time regime, accumulation at the interface becomes negligible, but copolymer continues to diffuse from phase I into phase II. This period may thus be described by a one-dimensional diffusion across an interface with no accumulation at the interface, and with a boundary condition $c_f(z = 0^+) = Kc_f(z = 0^-)$. The analytic solution to this problem[15] is

$$c_f(z,t) = \begin{cases} c_i^I + (c_0 - c_i^I)\mathrm{erf}(z/\sqrt{4D_f^I t}) & z > 0 \\ c_i^{II}\,\mathrm{erfc}(-z/\sqrt{4D_f^{II}t}) & z < 0 \end{cases} \tag{6}$$

This solution has the peculiar property that the concentrations $c_i^I \equiv c_f(z = 0^+)$ and $c_i^{II} \equiv c_f(z = 0^-)$ near the interface in both phases are independent of time, giving an interfacial coverage $\Gamma(t) = L^Ic_i^I$ that is also independent of time, though $c_f(z,t)$ changes everywhere else. This solution yields a flux $J_I(t)$ from phase I to the interface and a flux $J_{II}(t)$ from the interface into phase II, given by

$$J_I(t) = \sqrt{\frac{D_f^I}{\pi t}}(c_0 - c_i^I)$$

$$J_{II}(t) = \sqrt{\frac{D_f^{II}}{\pi t}}c_i^{II} \tag{7}$$

that both decrease as$1/\sqrt{t}$. By assuming the existence of time-independent interfacial concentrations, with $c_i^{II} = c_i^I/K$, and requiring that $J_I(t) = J_{II}(t)$ in the absence of interfacial accumulation, we obtain

$$c_i^I = \frac{c_0}{1 + \sqrt{P}} \tag{8}$$

where P is defined in eq 5. If $P \ll 1$ (or $\tau_{acc} \ll \tau_{leak}$) this yields a concentration $c_i^I \simeq c_0$ and a coverage $\Gamma \simeq \Gamma_0$ very close to their equilibrium values. If $P \gg 1$ (or $\tau_{leak} \ll \tau_{acc}$) this yields values $c_i^I \ll c_0$ and $\Gamma \ll \Gamma_0$ that are signficantly depressed by leakage into phase II. It is shown in what follows that a time-

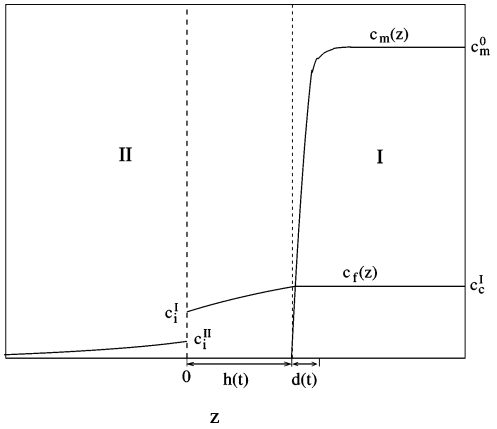

Figure 2. Schematic diagram of the concentration $c_f(z)$ of free copolymer in both phases and the micelle concentration $c_m(z)$ in phase I, for a system with an exclusion zone. The micelle concentration vanishes in the exclusion zone $0 < z < h(t)$, and is depleted in a region of width $d(t)$.

independent interfacial concentration is also obtained at intermediate times when micelles are present in phase I.

4. Micelles in Phase I, Early Times

In this section, we consider the initial stage of interfacial accumulation in a system in which $c_0 > c_c^I$, so that micelles are initially present in phase I. Throughout this section and the next, the analysis is limited to systems in which $\mu_c^I < \mu_c^{II}$, or $c_c^I/K < c_c^{II}$, so that the formation of micelles in phase I is preferred over the formation of micelles in phase II when the two phase are in equilibrium.

At $t = 0$, both Γ and c_i^I must vanish. At early times, while $c_i^I(t) = \Gamma(t)/L^I$ remain less than c_c^I, there must thus exist a region of some width $h(t)$ near the interface in which $c(z) < c_c^I$, in which there can be no micelles. In any system with $c_0 > c_c^I$, we may thus divide phase I at early times into an "exclusion zone" $0 < z < h(t)$ in which $c_f(z) < c_c^I$ and $c_m(z) = 0$, and a "micellar zone" $z > h(t)$ in which $c_f(z) = c_c^I$ and $c_m(z) > 0$.

A schematic of this behavior is shown Figure 2. As shown there, the micelle concentration $c_m(z)$ must vanish along the moving edge $z = h(t)$ of the exclusion zone. If $D_m^I \neq 0$, then, within the micellar zone $z > h(t)$, there will generally be a depletion region of some width $d(t)$ that precedes the edge of the exclusion zone, in which $c_m(z)$ is signficantly less than c_{m0}. Micellar diffusion is signficant only within this depletion region. For copolymer that starts in a micelle to reach the interface between phases I and II, it must first be transported by micellar diffusion to the moving edge of the diffusion zone, where micelles dissolve, and then undergo molecular diffusion across the exclusion zone.

4.1. Immobile Micelles. Consider the simple limit of vanishing micelle diffusivity ($D_m^I = 0$) and vanishing flux into phase II ($J_{II} = 0$). In this limit, there can be no diffusion in the micellar region, throughout which $c_m(z) = c_{m0}$. There will, however, be a gradient of $c_f(z)$ across the exclusion zone, since c_f must satisfy boundary conditions $c_f(z,t) = c_c^I$ at $z = h(t)$ and $c_f(z,t) = \Gamma(t)/L^I$ at $z = 0$. In the limit $D_m^I = 0$, the resulting flux of free copolymer across the exclusion zone must be provided by dissolution of micelles along the boundary $z = h(t)$. In this limit, the micellar zone is eaten away in a process analogous to that which occurs when a solid is immersed in a liquid in which it is soluble. The flux of free copolymers at $z = h(t)$ must thus equal the rate

$$J_I(t) = c_{m0}\frac{dh(t)}{dt} \tag{9}$$

at which micelles are dissolved along a moving boundary $z = h(t)$. If we make a quasi-steady state approximation, in which we assume negligible accumulation of copolymer within the depletion zone, and thus approximate $c_f(z)$ within the depletion zone by a linear function of z, the diffusive flux through this region is

$$J_I(t) = D_f^I\frac{c_c^I - c_i^I(t)}{h(t)} \tag{10}$$

Our model for the growth of $\Gamma(t)$ is completed by the boundary condition $c_i^I(t) = \Gamma(t)/L^I$ and, in the limit $J_{II}(t) = 0$, a balance equation $d\Gamma(t)/dt = J_I(t)$.

An asymptotic approximation for $h(t)$ at very early times, when $c_i^I(t)$ remains much less than c_c^I, may be obtained by approximating $c_i^I(t) \simeq 0$ in eq 10. By combining this with eq 9, and solving the resulting simple differential equation for $h(t)$, we obtain an exclusion zone width

$$h(t) \simeq \sqrt{2D_f^I t c_c^I/c_{m0}} \tag{11}$$

that grows as $\sqrt{t}$, and a flux

$$J_I(t) \simeq \sqrt{D_f^I c_c^I c_{m0}/(2t)} \tag{12}$$

Note that the time dependence of this solution is similar to that found in the absence of any micelles: The length $h(t)$ increases as $\sqrt{t}$, the flux decreases as $J_I(t) \propto 1/\sqrt{t}$ and the coverage increases as $\Gamma(t) \propto \sqrt{t}$.

If J_{II} is negligible, the $\sqrt{t}$ growth of Γ continues until Γ reaches a value $\Gamma_c = c_c^I L^I$. The width $h(t)$ of the exclusion zone approaches a corresponding final value $h_c = \Gamma_c/c_{m0}$, for which the total amount of material $h_c c_{m0}$ obtained from the dissolution of micelles equals the final interfacial coverage. This final state is reached over a time of order

$$\tau_{acc} = \frac{(L^I)^2}{D_f^I}\frac{c_c^I}{c_{m0}} \tag{13}$$

In the limit $D_m^I = 0$ and $J_{II} = 0$ considered here, the exact solution for $h(t)$ at all t may given as an implicit expression

$$\ln\left(1 - \frac{h(t)}{h_c}\right) + \frac{h(t)}{h_c} = -\frac{t}{2\tau_{acc}} \tag{14}$$

in which τ_{acc} is given by eq 13. This yields $h(t) \propto \sqrt{t}$ at $t \ll \tau_{acc}$, and an exponential approach of $h(t)$ to h_c at $t \gg \tau_{acc}$.

The analysis given in this subsection would apply equally well to situations in which copolymer aggregates into bilayers or other large aggregates with negligible diffusivity. In all such situations, copolymer can be transported to the interface only by dissolution of the aggregate and free molecule diffusion. In the limit of vanishing aggregate diffusivity *and* vanishing cmc, transport must cease.

4.2. Mobile Micelles. The above description asssumes that $D_m^I = 0$, and thus that $d(t) = 0$. It remains approximately valid in systems with $D_m^I \neq 0$ as long as the width $d(t)$ of the depletion region remains much less than the width $h(t)$ of the exclusion zone. In this limit of small micelle diffusivity, $d(t)$ may be estimated as follows: The gradient dc_m/dz of the micelle

concentration at the boundary $z = h(t)$ may be calculated by matching the diffusive flux $D_m^I(dc_m/dz)$ of micelles at the $z = h(t)$ to the total flux $J_I(t)$ given in eq 12. Approximating $dc_m/dz \simeq c_{m0}/d(t)$ and matching fluxes yields an estimated width

$$d(t) \sim h(t)/S \sim \sqrt{D_m^I t/S} \tag{15}$$

in which S is a dimensionless parameter

$$S \equiv \frac{D_f^I c_c^I}{D_m^I c_{m0}} \tag{16}$$

We thus obtain $d(t) \ll h(t)$ in the early time regime if $S \gg 1$.

We now consider the opposite extreme $h(t) \ll d(t)$, which (we now show) is obtained when $S \ll 1$. In this case, the edge of the exclusion zone acts as a nearly stationary absorbing boundary along a surface $z = h(t) \simeq 0$. In this limit, $c_m(z)$ may thus be approximated at $z \gg h(t)$ by the error-function solution that is obtained for an absorbing boundary at $z = 0$. This yields a depletion region of width

$$d(t) \sim \sqrt{4D_m^I t} \tag{17}$$

and a total flux

$$J_I(t) = c_{m0}\sqrt{\frac{D_m^I}{\pi t}} \tag{18}$$

The width of the exclusion zone may then be estimated in the limit $d(t) \gg h(t)$ by requiring that $J_I(t) = D_f^I c_c^I/h(t)$, while using eq 18 for $J_I(t)$. This yields $h(t) \sim Sd(t)$, thus confirming that $h(t) \ll d(t)$ when $S \ll 1$. The time τ_{acc} to accumulate a coverage Γ_c in the limit $J_{II} = 0$ is on the order of

$$\tau_{acc} \equiv \frac{(L^I)^2}{D_m^I}\left(\frac{c_c^I}{c_{m0}}\right)^2 \tag{19}$$

when $S \ll 1$.

4.3. Flux into Phase II. The effects of a nonzero flux into phase II at early times in a system with micelles in phase I may described by arguments closely analogous to those given in subsection 3.1 for a system with no micelles. Because $c_i^{II}(t) = 2J_I(t)t/L^{II} \propto \sqrt{t}$ and $J_{II}(t) = c_i^{II}\sqrt{D_f^{II}/t}$ whether or not micelles are present, eq 3 still applies at early times when micelles are present. It still predicts $J_{II}(t) \sim J_I(t)$ at the time τ_{leak} given in eq 4. As before, this prediction is valid only if τ_{leak} is less than the time τ_{acc} required to accumulate a coverage Γ_c in the limit $J_{II} = 0$.

In the limit $S \gg 1$, in which micelle diffusivity in phase I is negligible, the time τ_{acc} is given by eq 13. In this limit we can quantify the significance of leakage into phase II by a dimensionless quantity

$$R \equiv \frac{D_f^{II}}{D_f^I}\frac{c_c^I}{c_{m0}}\frac{1}{K^2} \tag{20}$$

such that $R \sim \tau_{acc}/\tau_{leak}$. For $S \gg 1$, leakage is expected to have a signficant effect on interfacial concentration at intermediate times if $R > 1$.

By comparing eqs 16 and 20, we find that leakage into phase II can have a large efffect on the interfacial concentration ($R \gg 1$) in systems with $K > 1$ and $S > 1$ only if $D_f^{II} \gg (D_f^I)^2/D_m^I$, where generically, $D_f^I \gg D_m^I$. This can occur only if the free molecule diffusivity in phase II is much greater than that in phase I. In systems of nearly balanced copolymers, for which the equilibrium interfacial tension is very small, however, even small suppressions in interfacial coverage can cause large fractional changes in interfacial tension.

In the opposite limit $S \ll 1$, in which the flux in phase I is controlled by micellar diffusion, the significance of flux into phase II is controlled by a quantity

$$Q \equiv \frac{D_f^{II}}{D_m^I}\left(\frac{c_c}{c_{m0}}\frac{1}{K}\right)^2 = RS \tag{21}$$

that is defined such that $Q \sim \tau_{acc}/\tau_{leak}$, where τ_{acc} is given by eq 19.

5. Micelles in Phase I, Intermediate Times

We next consider the intermediate time regime, during which the rate of interfacial accumulation becomes negligible, in systems in which $c_0 > c_c^I$, so that micelles are initially present in phase I. As in the previous section, we limit ourselves to systems in which $c_c^{II} > c_c^I/K$, so that micelles are never formed in phase II.

As in the case $c_0 < c_c^I$, the intermediate time regime may be described by the solution of a diffusion problem in a composite medium with no accumulation at the boundary. When $c_0 > c_c^I$, however, two qualitatively different situations can arise: One possibility is that the exclusion zone that is created at early times may persist in the intermediate time regime. It is also possible for the exclusion zone to close at intermediate times as a result of micellar diffusion, creating a state in which $c(z) > c_c^I$ and $c_f(z) = c_c^I$ throughout phase I.

5.1. Diffusion with No Exclusion Zone. We first consider the case in which it is assumed that $c(z) > c_c^I$ for all $z > 0$, so that there is no persistent exclusion zone at intermediate times. In this case, the flux into phase II is given by the solution of the diffusion equation with a constant concentration $c_i^{II} = c_c^I/K$ at $z = 0$, which yields

$$J_{II}(t) = \sqrt{\frac{D_f^{II}}{\pi t}}\frac{c_c^I}{K} \tag{22}$$

If this case, an equal flux of copolymer must carried to the interface by micellar diffusion alone. Postulating an error function profile for the micelle concentration $c_m(z)$ in phase I, with a diffusivity D_m^I and a time-independent micellar interfacial concentration $c_m(0^+)$ yields a micellar flux

$$J_m(t) = \sqrt{\frac{D_m^I}{\pi t}}[c_{m0} - c_m(0^+)] \tag{23}$$

that also decreases as $1/\sqrt{t}$. By equating the prefactors of $1/\sqrt{t}$ in eqs 22 and 23, we find

$$\frac{c_m(0^+)}{c_{m0}} = 1 - \sqrt{Q} \tag{24}$$

where $Q \equiv RS$ is the dimensionless parameter defined in eq 21.

A micellar concentration $c_m(0^+) > 0$ is obtained at the interface only for $Q < 1$. For $Q > 1$, the only possible solution is thus one with an exclusion zone, which is discussed in the

next subsection. The criteria $Q < 1$ is equivalent to the requirement that the flux that would be obtained by micelle diffusion to an absorbing boundary, with $c_m(0^+) = 0$, must exceed the rate of leakage of copolymer into phase II, as given by eq 22. Note that the condition involves the micellar diffusivity D_m^I in phase I and the molecular diffusivity D_f^{II} in phase II, but not the molecular diffusivity D_f^I in phase I. This is because no molecular diffusion occurs in phase I in this scenario. If the condition $Q < 1$ is satisfied, the concentration of free copolymer near the interface thus reaches the equilibrium value c_c^I at intermediate times.

5.2. Diffusion with an Exclusion Zone. If $Q > 1$, micelle diffusivity alone cannot provide the flux of copolymer into domain II needed to maintain a concentration $c_i^I = c_c^I$ at the interface. Instead, the concentration $c_f(z)$ must drop below the cmc, and cause an exclusion zone to persist. In this case, the concentration profile is described schematically by Figure 2.

Immobile Micelles. We first consider the case of nearly immobile micelles, or $d(t) \ll h(t)$. Our analysis of this limit at intermediate times is very similar to the analysis given in subsection 4.1 for a system with immobile micelles at early times. The flux across the exclusion zone is again given by eq 9. If we make a quasi-steady state approximation, and thus approximate $c_f(z)$ within the exclusion zone by a linear function of z, we obtain a flux

$$J_I(t) = c_{m0}\frac{dh}{dt} = D_f^I\frac{c_c^I - c_i^I(t)}{h(t)} \tag{25}$$

Postulating the existence of a solution in which $c_i^I(t)$ is independent of time yields a differential equation for $h(t)$, which has a solution

$$h(t) = \sqrt{2D_f^I t(c_c^I - c_i^I)/c_{m0}} \tag{26}$$

and a corresponding flux

$$J_I(t) = \sqrt{\frac{D_f^I}{2t}(c_c^I - c_i^I)c_{m0}} \tag{27}$$

The difference between this solution and that obtained at very early times by assuming that $c_i^I(t) \simeq 0$ is that, at intermediate times, c_i^I approaches a nonzero constant value due to leakage into flux II. In the absence of leakage into phase II, $c_i^I = c_c^I$, and $J_I(t) = 0$.

By matching the prefactor of $1/\sqrt{t}$ in the rhs of eq 27 to the corresponding prefactor on the rhs of eq 7 for the flux into domain II, we again obtain a solution with a time independent value for c_i^I. In this limit of immobile micelles, we find that the ratio $x \equiv c_i^I/c_c^I$ satisfies a quadratic equation

$$0 = \frac{2}{\pi}Rx^2 + x - 1 \tag{28}$$

in which R is defined by eq 20. The solution $x = (-1 + \sqrt{1+4R'})/2R'$, where $R' \equiv 2R/\pi$. approaches 1 when $R \ll 1$, and decreases as $x \simeq R^{-1/2}$ for $R \gg 1$. For $Q > 1$, we thus obtain a strongly depleted interfacial concentration $c_i^I \ll c_c^I$ when $R \gg 1$, and a nearly equilibrium coverage $c_i^I \simeq c_c^I$ when $R \ll 1$.

The quasi-steady state assumption of a linear concentration profile for $c_f(z)$ within the exclusion zone will be valid as long as $h(t)$ is much less than $\sqrt{D_f^I t}$. We see from eq 26 that this criterion is satisfied whenever $c_{m0} \gg c_c^I - c_i^I$. This assumption is always valid when the initial micelle concentration c_{m0} greatly exceeds c_c^I, but can be violated when c_0 is very near the cmc.

Mobile Micelles. When micelle diffusivity D_m^I is small but nonzero, the width $d(t)$ of the depletion region may be estimated by approximating $dc_m/dz \simeq c_{m0}/d(t)$ and matching the diffusive flux $D_m^I(dc_m/dz)$ of micelles to the edge of the exclusion zone to the total flux $J_I(t)$. This yields an estimated width

$$d(t) \sim h(t)/S' \tag{29}$$

where $S' \equiv (1 - x)S$. At intermediate times, we thus find $d(t) \ll h(t)$ if $S' \gg 1$.

In the opposite limit of a very narrow exclusion zone $h(t) \ll d(t)$, we may be approximate $c_m(z)$ by the error-function solution obtained for an absorbing boundary at $z = 0$. This yields a depletion region of width $d(t) \sim \sqrt{4D_m^I t}$ and a flux and a total flux

$$J_I(t) = \sqrt{\frac{D_m^I}{\pi t}}c_{m0} \tag{30}$$

as in the case $Q < 1$ in which no exclusion zone is formed. In this limit, the concentration c_i^I of free molecules at the interface may be obtained by matching eq 30 to eq 22 for $J_{II}(t)$. This yields a value

$$\frac{c_i^I}{c_c^I} = \frac{1}{Q} \tag{31}$$

for the dimensionless ratio $x = c_i^I/c_c^I$. Note that eq 31 always yields $c_i^I < c_c^I$, because $Q > 1$. The width $h(t)$ of the exclusion zone in this limit may then estimated by assuming a linear concentration profile for $c_f(z)$ for $0 < z < h(t)$, and setting $D_f^I(c_c^I - c_c^I)/h(t)$ equal to eq 30 for the total flux. This yields an exclusion zone of width

$$h(t) = S'\sqrt{\pi D_m^I t} \tag{32}$$

confirming that $h(t) \ll d(t)$ in the intermediate time regime when $S' \ll 1$.

6. An Exact Solution with an Exclusion Zone

We now present an exact solution for the concentrations of free molecules and micelles in phase I of a system with an exclusion zone and a constant concentration c_i^I at the interface. This solution may be used to describe the both very early times, for which $c_i^I \simeq 0$, and the intermediate time regime in systems with $Q > 1$, in which there exists a time-independent nonzero interfacial concentration. In this solution, all characteristic lengths, including the width $h(t)$ of the exclusion zone, are found to increase increase as $t^{1/2}$. The solution is mathematically similar to the solution of the so-called Stefan problem,[16] in which the boundary between a solid and liquid-phase moves as a result of solification, at a rate that is controlled by thermal diffusion of the heat released by solidification.

We consider a boundary value problem in which we specify a constant value c_i^I for the interfacial concentration of free molecules in phase I. We postulate a solution in which $h(t)$ increases as $\sqrt{t}$, as found in all of the approximate solutions discussed in previous sections. We thus assume that

$$h(t) = H_f\sqrt{4D_f^I t} = H_m\sqrt{4D_m^I t} \tag{33}$$

where H_m and H_f are undetermined constants, with $H_f/H_m = \sqrt{D_m^I/D_f^I}$.

The concentration $c_f(z,t)$ of free molecules in the exclusion zone $0 < z < h(t)$ is given in general by

$$c_f(z,t) = c_i^I + (c_c^I - c_i^I)\frac{\mathrm{erf}(Z_f)}{\mathrm{erf}(H_f)} \tag{34}$$

for $Z_f \le H_f$, where $Z_f \equiv z/\sqrt{4D_f^I t}$. Equation (34) satisfies the diffusion equation for free molecules, with the boundary conditions $c_f(0,t) = c_i^I$, and $c_f(h(t),t) = c_c^I$. The corresponding concentration of micelles is

$$c_m(z,t) = c_{m0}\frac{\mathrm{erf}(Z_m) - \mathrm{erf}(H_m)}{1 - \mathrm{erf}(H_m)} \tag{35}$$

in the micellar zone $Z_m \ge H_m$, where $Z_m \equiv z/\sqrt{4D_m^I t}$. Equation 35 is the solution of the diffusion equation with diffusivity D_m^I and boundary conditions $c_m(h(t),t) = 0$ and $c_m(\infty,t) = c_{m0}$.

The undetermined constant H_m must be chosen so as to satisfy the remaining boundary condition, which requires that the free molecule flux $J_f(z)$ in the exclusion zone $z < h(t)$ match the micellar flux $J_m(z)$ in the micellar zone $z > h(t)$ along the boundary $z = h(t)$. These fluxes are given by

$$J_f(z,t) = \sqrt{\frac{D_f^I}{\pi t}}(c_c^I - c_i^I)\frac{e^{-Z_f^2}}{\mathrm{erf}(H_f)}$$

$$J_m(z,t) = \sqrt{\frac{D_m^I}{\pi t}}c_{m0}\frac{e^{-Z_m^2}}{1 - \mathrm{erf}(H_m)} \tag{36}$$

in the domains $Z_f < H_f$ and $Z_m > H_m$, respectively. The requirement that $J_f = J_m$ at the boundary yields the condition

$$S(1 - x_i) = \beta\frac{1 - \mathrm{erf}(H_m)}{\mathrm{erf}(\beta H_m)}e^{-H_m^2}(1 - \beta^2) \tag{37}$$

where $\beta = \sqrt{D_m^I/D_f^I}$. To obtain a solution for the concentration profile for a system with a specified interfacial concentration c_i^I, eq 37 must be solved to obtain H_m.

To describe the initial accumulation of an interfacial layer at very early times, we approximate $c_i^I \simeq 0$ in the above. To describe intermediate times, we must choose c_c^I so as to equate the flux $J_f(0,t)$ to the interface to the corresponding flux J_{II} from the interface into phase II, which is given by eq 7. This condition yields an interfacial concentration

$$c_i^I = \frac{c_c^I}{1 + T} \tag{38}$$

where

$$T = \sqrt{\frac{D_f^{II}}{D_f^I}}\frac{\mathrm{erf}(H_f)}{K} \tag{39}$$

Substituting this relation for c_i^I into eq 37 reduces the problem again to that of solving a single nonlinear equation for $H_f = \beta H_m$. The two approximate solutions discussed in subsection 5.2 correspond to limits in which $H_m \gg 1$ and $H_m \ll 1$, respectively. Both assume that $H_f \ll 1$, or $h(t) \ll \sqrt{4D_f^I t}$, which is required to obtain an approximately linear concentration profile in the exclusion zone, and is generally correct as long $D_f^I \ll D_m^I$.

Aside from its usefulness as the basis of a numerical solution, the existence of this similarity solution proves that the width of the exclusion zone, when one exists, always grows as $\sqrt{t}$ at both early and intermediate times, and that the interfacial concentration c_i^I is rigorously independent of time in the intermediate time regime.

7. Micelle in Phase I, Thermodynamic Inversion

Consider a different situation, in which we initially mix copolymer in what is, from a thermodynamic point of view, the wrong phase: Let the copolymer be initially mixed homogeneously throughout phase I with a concentration $c_0 > c_c^I$, so that micelles are formed, but let $\mu_c^{II} < \mu_c^I$ or $c_c^{II} < c_c^I/K$, so that in a global equilibrium state micelles can appear only in phase II. This might occur, for example, if one mixed a diblock copolymer with $f_A < {}^1/_2$ into a phase of nearly pure A, forcing the formation of inverted micelles in which the B core block is longer than the A corona, and then tracked the diffusion of the copolymer into the B phase. In this section, I restrict myself to a discussion of intermediate and late times.

In this case, the concentration c_i^{II} of free molecules in phase II near the interface can never exceed the critical micelle concentration c_c^{II}. As a result, the interfacial concentration c_i^I in phase I can never exceed $c_c^{II}K$. Since, by assumption, $c_c^{II}K < c_c^I$, the concentration c_i^I in phase I must remain below c_c^I. In this case there must thus always be a persistent exclusion zone near the interface in phase I.

Two possibilities remain in the intermediate time regime: One possibility is an interfacial concentration $c_i^{II} < c_c^{II}$. In this case no micelles appear in phase II at intermediate times. The other possibility is one in which $c_i^{II} = c_c^{II}$, and in which micelles appear in phase II near the interface at intermediate times.

When no micelles are present in phase II, the mathematical model needed to describe the intermediate time regime is identical to that developed in subsection 5.2 to describe the situation in which there is an exclusion zone in phase I ($Q > 1$) and no micelles in phase II, but in which $c_c^{II} > c_c^I/K$. The only distinction between the two situations is the value of c_c^{II}, which is irrelevant if no micelles are formed phase II.

Micelles will appear in phase II near the interface at intermediate times if the model that neglects this possibility predicts an interfacial concentration $c_i^{II} \ge c_c^{II}$, or $c_i^I \ge c_c^{II}K$. Simplified criterion can be obtained in some limits. In the limit $S \gg 1$ in which $h(t) \gg d(t)$ in phase I, we find by setting $c_i^{II} \ge c_c^{II}$ in eq 28 that micelles appear when

$$\frac{2}{\pi}\frac{D_f^{II}}{D_f^I}\frac{c_c^{II}}{c_{m0}K} + 1 < \frac{c_c^I}{Kc_c^{II}} \tag{40}$$

Note that $c_c^I/Kc_c^{II} > 1$ by assumption, so the rhs always exceeds one. In the opposite limit $S \ll 1$, we find from eq 31 that micelles form when $Q < c_c^I/(c_c^{II}K)$, or

$$\sqrt{\frac{D_f^{II}}{D_m^I}\frac{c_c^I}{c_{m0}K}} < \frac{c_c^I}{c_c^{II}K} \tag{41}$$

In either limit, the formation of micelles within phase II near the interface is favored by a low value of D_f^{II}, since a high diffusivity in phase II tends to suppress c_i^{II} by sweeping copolymer away from the interface. If micelles do appear in phase II near the interface, the chemical potential of copolymer at the interface again reaches the maximum value allowed by thermodynamics, which in this case corresponds to a concentration $c_i^{II} = c_c^{II}$, during a time regime in which most of phase II contain no copolymer. Intentionally mixing copolymer with the "wrong" phase, in which it forms inverted micelles, may thus be a useful strategy for establishing an equilibrium copolymer chemical potential at the interface.

If micelles do appear near the interface in phase II, the micellar zone and exclusion zone that exist in phase I must be repeated in phase II, in reverse: There must a micellar zone near the interface in phase II, within which $c_m(z) > 0$ and $c_f(z) = c_c^{II}$, and a semi-infinite micelle-free zone further from the interface, within which $c_m(z) = 0$ and $c_f(z) < c_c^{II}$. In this case, transport of copolymer between the two phases must thus involve micellar diffusion to the edge $z = h(t)$ of the exclusion zone in phase I, dissolution of the micelles at this edge, molecular diffusion across the exclusion zone, re-formation of micelles on the phase II side of the interface, micellar diffusion across the micellar zone in phase II, dissolution of the micelles at the edge of the micellar region in phase II, and molecular diffusion into the micelle-free interior of phase II.

The evolution of such a system over very long times can follow different scenarios, depending upon the relative volumes of phases I and II and the initial concentration of copolymer in phase I. The simplest scenario is for the micellar region of phase II to expand until it fills all of phase II, the micelle-free region region in phase I to expand until it fills phase I, and transport of free copolymer from phase I to phase II to then continue until the concentration in phase I reaches $c_f = c_c^{II}K$ throughout. This would leave the system in a final state in which there are micelles throughout phase II and none in phase I. A different scenario must occur, however, if the excess of the initial copolymer concentration above $c_c^{II}K$ in phase I is insufficient to fill phase II at a homogeneous concentration c_c^{II}, i.e., if $c_0 - c_c^{II}K$ times the volume of phase I is less than c_c^{II} times the volume of phase II. In this case, the final state will contain no micelles in either phase, and so any micelles that form in phase II near the interface at intermediate times must ultimately redissolve.

8. Conclusions

The combination of diffusion and micellization can lead to nontrivial transport phenomena near an interface. In the diffusion-limited situation considered here, an exclusion zone with no micelles must be formed near an initially bare interface, because the local concentration must initially be depressed below the cmc. As long as the exclusion zone persists, transport to the interface must occurs by a combination of free molecule diffusion within this zone and micellar diffusion in the "micellar" region farther from the interface. The resulting flux to the interface may be controlled either by free molecule diffusion, when the cmc is not too far below the initial copolymer concentration ($S \gg 1$), or by micellar diffusion, when the cmc is very small ($S \ll 1$).

If the copolymer has a solubility in phase II comparable to that in phase I (i.e., if K is not too large), then there will exist an intermediate time regime during which copolymer is transferred from one phase to the other, but in which the rate of interfacial accumulation is negligible. During this period, the copolymer chemical potential is found to be independent of time. This has long been known to be true for diffusion of free molecules between two semi-infinite media,[15] in the absence of micellization. Here, it is shown that it remains true even when micelles form, under surprisingly general conditions.

During the intermediate time regime, the chemical potential at the interface may or may not correspond to that obtained in equilibrium above the cmc. If the solubility and/or diffusivity of free copolymer in phase II are sufficiently high, or the initial concentration of copolymer sufficiently low, such that $Q > 1$, then the copolymer concentration near the interface will be depressed below the cmc, creating an exclusion zone, and a depressed interfacial coverage. If the solubility and/or diffusivity in phase II are sufficiently low, or the initial concentration sufficiently high, such that $Q < 1$, the concentration near the interface will remain above the cmc, and interfacial coverage will reach its equilibrium value relatively quickly.

In systems of sufficiently asymmetric diblock copolymers, with a partition coefficient $K \gg 1$, the flux into phase II will always be negligible, yielding $Q < 1$, as a result of the strong thermodynamic preference for phase I. The tendency of diffusion into phase II to depress the interfacial coverage is, however, potentially relevant in systems of symmetric or nearly symmetric diblock copolymers, for which $K \sim 1$.

For simplicity, several potentially important phenomena have been neglected in the above:

Micelle Dissolution Kinetics. One key element in the above analysis is the assumption of local equilibrium between micelles and free molecules. This is equivalent to an assumption of rapid reaction rates for micelle dissolution and creation near the cmc. Semenov,[1] using a strong stretching theory to describe both the equilibrium micelle and the transition state, argued that there will instead often be a large barrier for the creation and destruction reaction at the cmc for typical copolymer molecular weights. The magnitude of the predicted kinetic barrier at the cmc depends strongly upon the molecular weight of the copolymer core block, however, and can be made modest for sufficiently low molecular weights. The barrier to dissolution may also be shown to depend sensitively upon the concentration of free molecules: A dissolution reaction that is extremely slow at the equilibrium cmc may proceed rapidly below a somewhat lower concentration, producing phenomena similar to those described here, except for the replacement of the equilibrium cmc by a kinetically controlled "apparent" cmc. The assumption of fast micelle dissolution kinetics at the cmc is probably correct only for rather short copolymers, but may be appropriate to some of the low molecular weight model systems used in interfacial tension measurements, as discussed below.

Emulsification. Near the interface, micelles of A−B copolymers in an A matrix will tend to swell by emulsifying B homopolymer within the micelle core.[17] The extent of swelling in the nonequilibrium situation discussed here must depend upon distance from the interface, and upon the solubility of B homopolymers within an A matrix, because the emulsification of B homopolymer within a micelle can only occur by diffusion of dissolved B homopolymer through the surrounding A phase. Far from the interface, micelles must remain unswollen. Near the interface, micelles may not be able to swell to their equilibrium radii before dissolving, due to diffusion limitations. Because the equilibrium interfacial tension is quite sensitive to the extent of micelle swelling,[17] this issue may merit further consideration.

Form of Aggregate. The above discussion assumed a nonnegligible micelle diffusivity. This makes sense only if the

copolymer aggregates in phase I into dispersed spherical micelles, or short rods. Copolymer could, of course, also assemble into long cylindrical micelles, bilayers, or aggregates of spheres, cylinders or bilayers. The formation of spherical micelles is expected only for sufficiently asymmetric diblock copolymers or for nearly symmetric copolymers of sufficiently low molecular weight in low molecular weight homopolymer, for which the corona swells signficantly. Use of copolymers in which the corona block molecular weight is significantly lower than that of the matrix homopolymer can, however, lead to aggregation of micelles or bilayers into a separate copolymer rich phase, as the result of an entropic attraction between polymer brushes in high-molecular weight matrix (see, e.g., the self-consistent field study by Thompson and Matsen,[18] and references therein). The analysis given in section 4.1 of transport by free molecule diffusion in the limit of negligible micelle diffusivity may be a useful starting point for analyzing such situations, in systems for which the coexisting concentration of free molecules (i.e., the cmc) is not also negligible.

The analysis given here was motivated by measurements by K. Chang[14] of the interfacial tension of A/B interfaces in the presence of low molecular weight symmetric and moderately asymmetric A-*b*-B diblock copolymers. These experiments used low molecular weight diblocks, in which the core block had molecular weights of 5−10 kDa and $\chi N_{core} \sim 10$, with homopolymers of molecular weights less than or equal to that of the copolymer corona block. Such systems are a natural starting point for studying the effect of copolymer upon interfacial tension γ, because symmetric and nearly symmetric diblocks are predicted to dramatically reduce γ in equilibrium, and because the use of low molecular weight polymers helps minimize various possible kinetic limitations.

The analysis given here appears to be an appropriate starting point for understanding such experiments. It provides an estimate of the time τ_{acc} required to accumulate a monolayer by a combination of free molecule and micellar diffusion. It shows that, for nearly symmetric diblock copolymers, the observation of a time-independent interfacial tension does not necessarily indicate that an equilibrium interfacial tension has been obtained. It predicts that the desired equilibrium value for a micellar solution can, however, be obtained at concentrations above an apparent cmc, above which $Q < 1$. This apparent cmc is predicted to always be greater than the true cmc (because Q diverges as $c_{m0} \rightarrow 0$), with a value that depends upon transport parameters in both phases. The apparent cmc will be much closer to the true cmc when the copolymer is added to the homopolymer in which it has a higher diffusivity. Evidence of the existence of such a nonequilibrium apparent cmc has been obtained by Chang in experiments on systems of polystyrene (PS), polybutadiene (PB), and symmetric PS-*b*-PB block copolymer.[14] These will be reported elsewhere.

Some aspects of the present analysis are also relevant to the study of copolymer transport in compatibilized immiscible polymer blends, if a premade copolymer is initially mixed into one of the two immiscible homopolymers. The separation between the time required to accumulate a monolayer and the time required to repartition copolymer between phases will generally be small or nonexistent in such blends, because of the small domain sizes, on the order of 1−10 μm, that are often produced by mechanical mixing. If the amount of copolymer added to a blend is chosen so as to saturate the amount of interface produced by mixing, with little copolymer left in micelles, then the time required to saturate the interface is essentially the same as the time required for copolymer diffuse to the interface from the entire volume of the phase to which it is initially added. The notion of an intermediate time regime will thus usually not be relevant in this context. The notion of an exclusion zone and the description of the interplay of free molecule and micellar diffusion at early times are, however, potentially relevant to the analysis of copolymer transport during blending.

The analysis presented here provides only a partial answer to the general question of how and how fast copolymer will be transported to a polymer/polymer interface after forming micelles or other aggregates within a homopolymer phase. The most important omissions are the probably the assumptions of rapid micelle dissolution and of rapid interfacial adsorption and deadsorption of individual chains. For all but rather small copolymers, limitations on the rates of these "reactions" will limit transport to the interface[1] and so should be the focus of further work along these lines.

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