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Diblock Copolymer Surfactants in Immiscible Homopolymer Blends: Swollen Micelles and Interfacial Tension

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ABSTRACT: We consider the effect of micellization upon the equilibrium macroscopic interfacial tension between A- and B-rich phases in a ternary mixture of immiscible A and B homopolymer with an AB diblock copolymer surfactant, for systems in which spherical micelles can form in the A-rich phase. Self-consistent field theory (SCFT) has been utilized to calculate the critical micelle concentrations (cmc's) and macroscopic interfacial tensions. The behavior of the systems of nearly balanced copolymers, which tend to form highly swollen micelles, is discussed within the context of the Helfrich theory of bending elasticity, using elastic constants obtained from SCFT simulations of weakly curved monolayers.

1. Introduction

Diblock copolymers are often used as surfactants in blends of immiscible homopolymers. AB diblock copolymers adsorb at interfaces between the A and B homopolymer domains, and they stabilize the dispersion of the minority homopolymer by reducing interfacial tension, which promotes droplet breakup, and by suppressing droplet coalescence.[1,2] The extent of interfacial adsorption is limited by micellization: Once the concentration of dissolved copolymer exceeds the critical micelle concentration (cmc) in either phase, additional block copolymer is used to form micelles, preventing further increase in the interfacial coverage of copolymer and any further decrease in the interfacial tension.

Although micellization always competes with interfacial adsorption in immiscible blends, most theoretical studies of these phenomena have focused either on interfacial adsorption, while ignoring the possibility of micellization,[3,4] or on predictions of the cmc in binary mixtures of copolymer in a single homopolymer.[5−10] The exception to this rule is a study by Leibler,[11] who considered the saturation of interfacial tension γ above the cmc. Leibler used simple strong-stretching theory to describe both micelles and an adsorbed monolayer, and calculated the macroscopic interfacial tension by equating the chemical potential of copolymer adsorbed to the interface with that in the micelles. He came to the puzzling conclusion that the macroscopic interfacial tension in immiscible blends with nearly symmetric copolymers could be driven to zero at copolymer concentrations below the cmc, for copolymers with a rather wide range of values $f_A = 0.31-0.69$ of the volume fraction f_A of the A-block. However, Leibler estimated the free energy of formation of a micelle using a model appropriate to a binary system of copolymer in a homopolymer matrix. He thus neglected the fact that a micelle in an A-rich phase that coexists with an excess phase of nearly pure B homopolymer can swell by emulsifying B homopolymer within its core.

In this article, we use numerical self-consistent field theory (SCFT) to examine how the formation of swollen spherical micelles limits the reduction of macroscopic interfacial tension. Our description of the limit of very highly swollen micelles, or (equivalently) droplet microemulsions,[13,14] is based on the Helfrich theory of interfacial bending elasticity. Allowing the micelles to swell generally reduces the calculated free energy of formation of a micelle. This reduces the predicted cmc, and thus it raises the limiting value of γ reached above the cmc. In contrast to Leibler, we find that the concentration of free copolymer needed to drive the interfacial tension to zero is always greater than or (for balanced surfactants) equal to the predicted cmc. We thus generally obtain a nonzero interfacial tension above the cmc.

Though detailed results are given only for systems in which spherical micelles form in one of two coexisting phases, we also discuss when any of several competing structures might form instead. In addition, we discuss attempts to use the Helfrich theory to describe bicontinuous microemulsion phases, and how the formation of a bicontinuous (rather than droplet) microemulsion might affect the macroscopic interfacial tension.

2. Theory. Micellization

We consider a ternary system of two immiscible homopolymers, A and B, and an AB diblock copolymer (denoted C), under condition for which system phase separates into two phases rich in A and B, respectively, with a small concentration of copolymer C. Let N_A, N_B, and N_C denote the degrees of polymerization of the two homopolymers and copolymer, respectively, and f_A denote the volume fraction of A monomers within the copolymer. Let $\alpha_A \equiv N_A/N_C$, $\alpha_B \equiv N_B/N_C$, and $\beta \equiv N_A/N_B$. For specificity, we consider the case in which, above the critical micelle concentration, spherical micelles preferentially form in the A-rich phase. In the case of symmetric homopolymers with $\beta = 1$ and equal statistical segment lengths $b_A = b_B$, this corresponds to the case $f_A > {}^1/_2$.

2.1. Phenomena. The dilute region of the ternary phase diagram for such a system is shown schematically in Figure 1. The copolymer is assumed to form micelles in the A-rich phase above the cmc line, shown by the dotted line $c-b$, which extends from the cmc of the binary A−C system (point c) to the cmc of an A-rich phase that coexists with a B-rich phase (point b). The dash−dotted tie line that intersects the phase boundary at point b divides the two-phase region into a lower region of very

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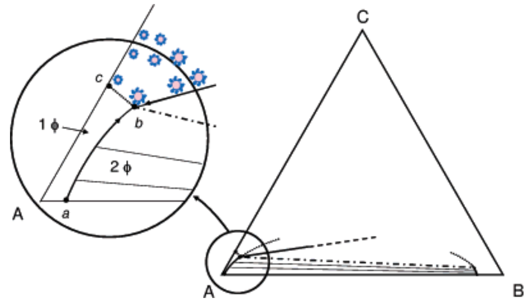

Figure 1. Schematic phase diagram of a ternary system comprised of homopolymers A and B and diblock copolymer C, in which an A-rich phase of swollen micelles (or, equivalently, microemulsion droplets) coexists with a phase of nearly pure B. The dotted line *b*−*c* is a line of the critical micelle concentration in a single A-rich phase. Micelles are drawn above this line. A point *b* corresponds to the cmc in two-phase ternary system.

low copolymer concentration in which neither of the two coexisting phases contains micelles, and an upper region of higher copolymer concentration in which a micellar A-rich phase coexists with a micelle-free B-rich phase. Below this cmc tie-line, the boundaries of the A-rich and B-rich phases are reasonably well described by Flory−Huggins theory. Above the cmc, the solubility of B within the micellar phase becomes higher than that predicted by Flory−Huggins theory, as a result of the solubilization of the B homopolymer within the cores of swollen micelles. The slope of the phase boundary of the A-rich phase above the cmc (the emulsification failure line) reflects the ratio of surfactant to emulsified B within a micelle, which yields a lower slope for more highly swollen micelles.

The chemical potential μ_C of copolymer within the A-rich phase is related by a dilute solution law,

$$\mu_C = \mu_C^0 + kT \ln(\rho_C^f/\rho_C^0) \tag{1}$$

to the number concentration ρ_C^f of free copolymers dissolved as single molecules (rather than within micelles) within the A-rich phase. Here, ρ_C^0 is a standard state concentration, and μ_C^0 is a corresponding standard state chemical potential for free copolymer dissolved in A. A similar relation exists between the chemical potential μ_B of B homopolymer and the concentration of free B molecules dissolved in the A-rich matrix. Above the cmc, the concentrations and the corresponding chemical potentials of free B and C molecules within the A matrix in a two-phase system always remain very close to those obtained at the cmc. The resulting saturation of ρ_C^f (or the volume fraction ϕ_C^f) and μ_C to nearly constant values are shown schematically in Figures 2 and 3. In a two-phase system, micelles generally form in only one phase (here, the A-rich phase) because the saturation of μ_C caused by micellization in the A-rich phase prevents μ_C from ever reaching the higher value required for micellization in the B-rich phase.

Interfacial tension γ of a macroscopic interface between coexisting A- and B-rich phases monotonically decreases with increasing μ_C while the interfacial coverage of adsorbed copolymer increases. As shown in Figure 4, interfacial tension extrapolates to zero at a saturation chemical potential μ_C^* or a corresponding concentration ρ_C^* of free dissolved copolymer. If μ_C^{cmc} is less than the saturation chemical potential μ_C^*, then γ will decrease only until the cmc is reached, and thereafter remain very close to the nonzero value γ_{cmc} obtained at the cmc. If μ_C^{cmc} were somehow to exceed μ_C^*, however, then it would be possible to drive the interfacial tension to zero at a copolymer concentration below the cmc.

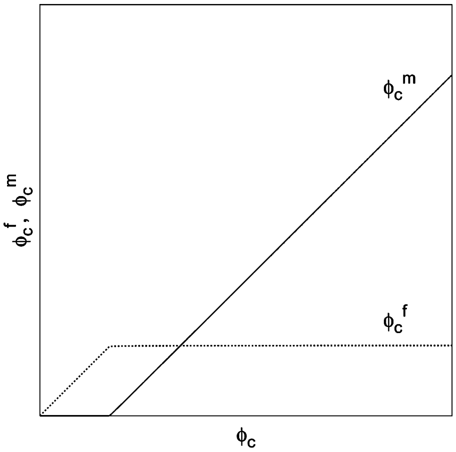

Figure 2. Concentration dependence of free copolymer ϕ_C^f and of copolymer within micelles ϕ_C^{m} upon the total concentration of copolymer within the micellar phase ϕ_C, along the coexistence line.

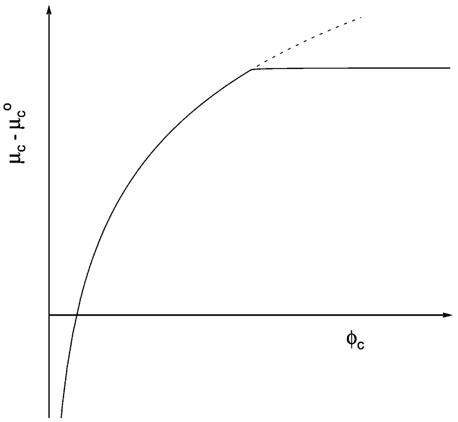

Figure 3. Dependence of the copolymer chemical potential upon total concentration of copolymer within the micellar phase, along the coexistence line. The dotted line shows the continuation of ideal solution behavior beyond the cmc.

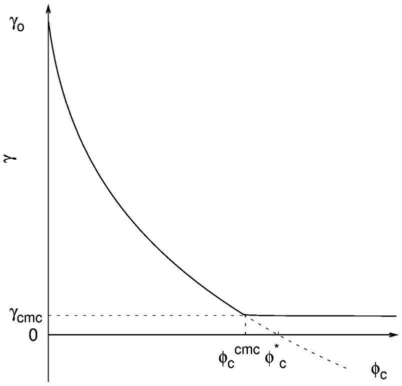

Figure 4. Schematic diagram of the macroscopic interfacial tension γ vs the total volume fraction of copolymer within the A-rich micellar phase. As in Figure 3, the solid line shows the behavior of a micellar solution, and the dotted line shows the continuation of ideal solution behavior, in the absence of micelles.

Leibler estimated μ_C^* and μ_C^{cmc} from the free energies of flat interfaces and spherical micelles using a simple strong-stretching calculation. Leibler found $\mu_C^{\mathrm{cmc}} < \mu_C^*$ for sufficiently asymmetric copolymers, with $|f_A - 0.5| > 0.19$, but $\mu_C^* < \mu_C^{\mathrm{cmc}}$ for more symmetric copolymers, with $0.31 < f_A < 0.69$. These calculations suggested that it should be possible to produce macroscopic interfaces with $\gamma = 0$ using block copolymers with a rather wide range of values of f_A. The most important limitation of Leibler's calculation, as noted in the Introduction, is that he did not allow for the possibility of swelling of the micelle cores. The nearly symmetric copolymers for which Leibler found $\mu_C^* < \mu_C^{\mathrm{cmc}}$, however, also form monolayers with large spontaneous radii of curvature and thus would tend to form highly swollen micelles. We show in what follows that, if the micelles of nearly symmetric copolymers are allowed to swell to their preferred size, μ_C^{cmc} always remains less than or equal to μ_C^*, causing the macroscopic interfacial tension to always saturate to a nonnegative value.

2.2. Thermodynamics. It is convenient to formulate both the classical thermodynamics of this system and the corresponding SCFT calculations in a grand canonical ensemble. The grand canonical free energy Φ of a system is given by the difference $\Phi \equiv F - \Sigma_i \mu_i M_i^{\mathrm{tot}}$, where F is the Helmholtz canonical free energy. Here, μ_i is the chemical potential and M_i^{tot} is the total number of molecules of species i in the system of interest, for i = A, B, C. For any macroscopic system of volume V and pressure P, $\Phi = -PV$. The interfacial tension γ of a flat macroscopic interface between A- and B-rich phases is conveniently expressed as an excess grand canonical free energy per unit interfacial area.

The grand canonical free energy of a dilute solution of micelles at a specified set of chemical potentials and a specified number density ρ_m of nearly monodisperse micelles may be expressed as a function

$$\frac{\Phi}{V} = -P^h(T,\mu) + \rho_m[\Phi^m(T,\mu) + kT\ln(\rho_m/\rho_m^{\,0}e)] \quad (2)$$

where P^h is the pressure of a hypothetical homogeneous (i.e., micelle-free) phase at the specified set of chemical potentials, and $\Phi^m(T,\mu)$ is the extrapolated excess grand canonical free energy per micelle of a hypothetical micellar solution with a standard state micelle concentration $\rho_m^{\,0}$. Here and hereafter, we use μ, with no subscripts, to refer to a set of chemical potentials $\mu \equiv \{\mu_A,\mu_B,\mu_C\}$. The true equilibrium grand canonical free energy at a specified T and μ is obtained by minimizing eq 2 with respect to variations in the number density ρ_m of micelles, which yields

$$\rho_m = \rho_m^{\,0}\exp[-\Phi^m(T,\mu)/kT] \quad (3)$$

Substituting this back into eq 2 produces a macroscopic pressure $P \equiv -\Phi/V = P^h + \rho_m kT$ in which the micelles contribute a small ideal-solution osmotic pressure of $\rho_m kT$.

In eq 2, we have not attempted to account separately for different "species" of micelles containing different numbers of molecules of copolymer or solubilized B homopolymer. The free energy $\Phi^m(T,\mu)$ should thus be understood to be an excess grand canonical free energy of a micelle of fluctuating size and composition. The numbers of copolymer and homopolymer molecules within each micelle can fluctuate by exchanging molecules between the micelle and the surrounding matrix. Correspondingly, ρ_m is the number density of micelles of any size or composition. This formulation assumes that it is possible to count the total number of micelles in any microscopic state of a micellar solution with little ambiguity, but it does not require us to define conventions for deciding how many molecules of each type reside "within" each micelle, and how many are part of the surrounding matrix.

Let the excess aggregation number of species i within a micelle, denoted M_i, be defined to be difference between the average number of molecules of species i in a system (or simulation) that contain exactly one micelle and that in a system of equal volume and equal chemical potentials with no micelles. These excess aggregation numbers are related to the corresponding excess free energy Φ^m by the thermodynamic identity

$$M_i = -\frac{\partial\Phi^m(T,\mu)}{\partial\mu_i} \quad (4)$$

In an incompressible fluid, the excess aggregation numbers for the three species are related by the fact that the total number of monomers are conserved regardless of the introduction of a micelle so that they must satisfy $0 = \Sigma_i N_i M_i$ for i = A, B, C. This definition thus yields positive values for the copolymer excess M_C, and (in an A-rich phase) for the excess M_B of solubilized B, but negative values for the "excess" M_A of matrix homopolymer.

2.3. Critical Micelle Concentration. A useful approximation for the critical micelle concentration may be obtained by neglecting the translational entropy of the micelles, and thus ignoring the logarithmic term in eq 2. In this approximation, the formation of micelles is favorable whenever $\Phi^m(T,\mu) \leq 0$. The cmc line ($b-c$) in Figure 1 thus corresponds in this approximation to the set of chemical potentials for which

$$0 = \Phi^m(T,\mu) \quad (5)$$

The thermodynamic analysis of micellization in this approximation is closely analogous to the analysis of a limit of solubility of a solid in a dilute liquid solution, in which any material added beyond the limit of solubility precipitates into a second phase.

When the translational entropy of the micelles is taken into account, the critical micelle concentration ceases to be a sharp phase transition. Instead, the cmc marks the position of a rapid but mathematically continuous crossover, which approaches the behavior of a true phase transition in the limit of infinitely large micelles. For finite micelles, the definition of the cmc is thus necessarily somewhat arbitrary. We choose to define the cmc of copolymer to be the concentration of free copolymers at the chemical potential μ_C^{cmc}, for which the concentration of unimers is equal to that of copolymers within micelles, i.e., for which

$$\rho_C^{\mathrm{cmc}} = \rho_C^f = \rho_m M_C \quad (6)$$

By substituting this definition into eq 3, we find that

$$0 = \Phi^m + kT\ln(\rho_C^{\mathrm{cmc}}/\rho_m^{\,0}M_C) \quad (7)$$

at the cmc, where $\Phi^m(T,\mu)$ is evaluated at the chemical potential for which $\rho_C^f = \rho_C^{\mathrm{cmc}}$.

In numerical SCFT calculations, in which Φ^m is taken to be the result of SCF calculations of the excess free energy of an isolated micelle, we take the standard state concentration $\rho_m^{\,0}$ to be the hypothetical state in which the volume fraction of copolymer within micelles extrapolates to unity, i.e., $\rho_m^{\,0} \simeq 1/(vN_C M_C)$, where vN_C is the volume per copolymer chain. This choice is obviously somewhat arbitrary. The calculated cmc is, however, found to be insensitive to all but enormous changes in the value of $\rho_m^{\,0}$, or to the neglect of micelle translational entropy entirely, for micelles of the size considered here. By using eq 4 and a linear approximation for the dependence of Φ^m on μ_C near the cmc, it is straightforward to show that the value obtained for μ_C at the cmc by solving eq 7 differs from that obtained from approximation eq 5, in which we completely neglect micelle translational entropy, by an amount $\delta\mu_C \simeq kT\ln(\rho_C^{\mathrm{cmc}}/\rho_m^{\,0}M_C)/M_C$. The corresponding shift in the calculated cmc ρ_C^{cmc}, vanishes in the limit $M_C \gg 1$, and has been found to correspond to a very small fractional change in ρ_C^{cmc} for the systems considered here.

2.4. Interfacial Model. To relate the thermodynamics of a highly swollen micelle to the bending elasticity of the monolayer that surrounds the core of each such micelle, it is useful to formally decompose the free energy of the micelle into core and interfacial components. For a spherical or cylindrical micelle of radius R, we imagine constructing a spherical or cylindrical Gibbs dividing surface of radius R and area A around the center of an isolated micelle. This surface separates an A-rich matrix (region I) from a B-rich core (region II). When the core is large, it has a composition similar to that of the coexisting B-rich phase. The excess free energy $\Phi^{\mathrm{m}} \equiv \Phi + P_{\mathrm{I}}V$ of a micelle with a core region of volume $V_{\mathrm{II}} = V - V_{\mathrm{I}}$ in a system containing one micelle in a total volume V may be expressed as a sum

$$\Phi^{\mathrm{m}} = (P_{\mathrm{I}} - P_{\mathrm{II}})V_{\mathrm{II}} + A\gamma \tag{8}$$

of the excess interfacial free energy $A\gamma$ plus an excess bulk free energy of the core that arises from the difference between the pressures in the core and matrix. The simplified criterion for the cmc, which we use throughout this section, requires that $\Phi^{\mathrm{m}} = 0$ at the cmc.

A criterion for the optimal micelle radius may be obtained by requiring that eq 8 for $\Phi^{\mathrm{m}}(R)$ be minimized with respect to changes in R at fixed values of all chemical potentials. The resulting criterion is equivalent to the condition for mechanical equilibrium of a curved interface,[12] and yields

$$P_{\mathrm{II}} - P_{\mathrm{I}} = C\gamma - \frac{C^2}{d-1}\frac{\partial\gamma}{\partial C} \tag{9}$$

where $C = (d - 1)/R$ is a mean curvature with $d = 3$ for a sphere or $d = 2$ for a cylinder.

In what follows, we approximate the macroscopic pressure in the A-rich micellar phase by the local pressure in the matrix. In doing so, we ignore the very small osmotic pressure $\rho_{\mathrm{m}}kT$ that arises in a dilute micellar phase from the translational entropy of the micelles. This is consistent with our neglect of micelle translational entropy in the criterion for the cmc. Because the chemical potentials of all components in the B-rich core of a swollen micelle must be the same as those in the coexisting B-rich macroscopic phase, the local pressure P_{II} within the core of a micelle must be equal to that in the coexisting B-rich phase. Because the pressures of the A- and B-rich phases must also be equal, and the pressure in the A-rich phase is taken to be equal to that of the matrix, the pressures in the core of a micelle must thus also equal that in the surrounding matrix, whenever the micellar phase coexists with an excess phase.

Combining the requirement that $P_{\mathrm{I}} = P_{\mathrm{II}}$ with the requirement that $\Phi^{\mathrm{m}} = 0$ in eq 8 yields a requirement that

$$\gamma = 0 \tag{10}$$

at the cmc of a two-phase system. Note that the vanishing interfacial tension in eq 10 is that of the curved monolayer surrounding a micelle, not that of the macroscopic interface between A- and B-rich phases, which is generally nonzero. Combining the conditions $P_{\mathrm{I}} = P_{\mathrm{II}}$ and $\gamma = 0$ with the mechanical equilibrium condition of eq 9 yields the additional requirement that

$$\left.\frac{\partial\gamma}{\partial C}\right|_{\mu} = 0 \tag{11}$$

Equation 11 reflects the fact that, when the micellar phase coexists with an excess B-rich phase, the optimal radius for a swollen micelle is that which minimizes the excess free energy per area of the curved monolayer around each micelle.

It is also interesting to consider the case of a one-phase micellar solution, in the absence of coexisting homopolymer phase. Combining eq 8 for Φ_{m} and eq 9 for the optimal radius yields

$$\Phi^{\mathrm{m}} = \frac{A}{d}\left[\gamma + C\frac{\partial\gamma}{\partial C}\right] \tag{12}$$

where $d = 3$ for a sphere or $d = 2$ for a cylinder. Applying the simplified cmc condition, $\Phi^{\mathrm{m}} = 0$, to this yields the requirement that

$$\gamma = -C\frac{\partial\gamma}{\partial C} \tag{13}$$

at the cmc. Substituting this back into eq 9 yields a pressure difference

$$P_{\mathrm{II}} - P_{\mathrm{I}} = -\frac{d}{d-1}C^2\frac{\partial\gamma}{\partial C} = \frac{d}{d-1}C\gamma \tag{14}$$

everywhere along the cmc line. In a one-phase micellar solution, the preferred micelle radius is restricted by a stoichiometric constraint on the amount of the available B homopolymer. This constraint causes the micelle interface to adopt a smaller radius, or higher curvature, than the spontaneous curvature that is reached along the emulsification failure line. This leads to a situation in which $\partial\gamma/\partial C > 0$, and in which a negative relative pressure $P_{\mathrm{II}} < P_{\mathrm{I}}$ develops in the core of each micelle. Along the cmc line, $b-c$ in Figure 1, the micelle radius is thus expected to decrease, and the pressure difference $P_{\mathrm{I}} - P_{\mathrm{II}}$ to increase, as one moves away from point b on the emulsification failure line, at which $P_{\mathrm{I}} = P_{\mathrm{II}}$, and toward point c of the binary A−C edge.

2.5. Helfrich Theory. The above division of the excess micelle free energy Φ^{m} into bulk and interfacial contributions is conceptually useful only for describing highly swollen micelles. When the radius of a swollen micelle becomes sufficiently large, the curvature dependence of the interfacial tension γ may be described by the Helfrich theory,[16] in which an interfacial excess free energy is expanded to harmonic order in powers of curvature. Here, we use a form of the theory discussed in more detail in another paper,[12] in which we expand γ about a flat saturated state (i.e., about $C = 0$, $\mu = \mu_C^*$, and $\gamma = 0$) for a spherical surface to harmonic order in powers of a curvature $C = 2/R$ and to linear order in the deviation $\delta\mu = \mu_C - \mu_C^*$.

Combining the Helfrich expansion of $\gamma(C,\mu_C)$ with eqs 10 and 11 yields

$$0 = \gamma = -\tau C + \frac{1}{2}\kappa_+ C^2 - \Gamma^*\delta\mu - \Lambda\delta\mu C \tag{15}$$

$$0 = \frac{\partial\gamma}{\partial C} = -\tau + \kappa_+ C - \Lambda\delta\mu \tag{16}$$

in which $\kappa_+ \equiv \kappa + {}^1\!/_2\bar{\kappa}$ is the bending rigidity for a spherically curved interface. In the limit of small τ, or small spontaneous curvature, eq 16 yields an equilibrium mean curvature

$$C \simeq \frac{\tau}{\kappa_+} \tag{17}$$

with corrections of $\mathcal{O}(\tau^2)$. In the same limit, eqs 15 and 16 yield a chemical potential shift

$$-\Gamma^*\delta\mu = \frac{1}{2}\kappa_+ C^2 \tag{18}$$

that vanishes in the limit $\tau \rightarrow 0$, or $C \rightarrow 0$.

The interfacial tension γ_{cmc} of a macroscopic flat interface between a micellar A-rich solution and an excess B-rich phase can be obtained by evaluating eq 15 with $C = 0$ and replacing $\delta\mu$ by eq 18. This yields a predicted interfacial tension

$$\gamma_{\mathrm{cmc}} = -\Gamma^*\delta\mu = \frac{1}{2}\kappa_+ C^2 \tag{19}$$

Combining eq 19 with eq 17 for C yields

$$\gamma_{\mathrm{cmc}} \simeq \tau^2/2\kappa_+. \tag{20}$$

The macroscopic interfacial tension is thus predicted to vanish at the balance point $\tau = 0$ and to vary quadratically with τ or spontaneous curvature $C \simeq \tau/\kappa_+$ near this point. Equation 20 for the interfacial tension is simply the free energy per unit area required to flatten a monolayer with the curvature $C = \tau/\kappa_+$ characteristic of an equilibrium micelle. As discussed by Strey,[24] this is because the macroscopic interfacial tension is the derivative of total free energy with respect to the area of the flat interface, and the additional surfactant required to increase the area of the flat interface must be provided by the destruction of micelles, thereby transferring surfactant from a curved monolayer to a flat one.

For nearly balanced monolayers, τ is expected to vary linearly with changes in any variable that can be used to tune monolayer asymmetry. In systems containing nonionic surfactant, in which temperature is a convenient control variable, there exists a balance temperature T_{m} at which $\tau = 0$, and $\tau \propto T - T_{\mathrm{m}}$ for T near T_{m}.[24] In an isothermal series of homologous polymeric mixtures with a specific pair of homopolymers, and a fixed value for either the copolymer length N_{C} or the length $f_{\mathrm{B}}N_{\mathrm{C}}$ of the core block, there will exist some copolymer composition $f_{\mathrm{A}}^{\mathrm{bal}}$ for which $\tau = 0$. If the homopolymers are symmetric, with $N_{\mathrm{A}} = N_{\mathrm{B}}$ and $b_{\mathrm{A}} = b_{\mathrm{B}}$, then $f_{\mathrm{A}}^{\mathrm{bal}} = {}^1\!/_2$. Within such a series, for values of f_{A} near $f_{\mathrm{A}}^{\mathrm{bal}}$, we expect a linear variation $\tau \simeq \tau'(f_{\mathrm{A}} - f_{\mathrm{A}}^{\mathrm{bal}})$, where the derivative $\tau' \equiv \partial\tau/\partial f_{\mathrm{A}}$ is evaluated at the balance point by slightly varying f_{A} while holding $f_{\mathrm{B}}N_{\mathrm{C}}$ or N_{C} constant, as appropriate for the series of interest with fixed N_{A}, N_{B}, b_{A}, b_{B}, and χ. Near the balance point, eq 19 may also be approximated as a quadratic function of f_{A}

$$\gamma_{\mathrm{cmc}} = \frac{(\tau')^2}{2\kappa_+}(f_{\mathrm{A}} - f_{\mathrm{A}}^{\mathrm{bal}})^2 \tag{21}$$

where κ_+ is evaluated at $f_{\mathrm{A}} = f_{\mathrm{A}}^{\mathrm{bal}}$.

The above analysis of a droplet microemulsion in coexistence with an excess phase is a slight refinement of ones given previously by Strey[24] and by Palmer and Morse.[13] These earlier analyses were both based on minimization of the Helmholtz free energy F, rather than of Φ, and required some simplifying assumptions of negligible surfactant solubility and/or negligible curvature dependence of the interfacial coverage that are not required in the formulation given here. The basic results are, however, the same.

3. SCFT Methodology

To study the effect of micellization upon macroscopic interfacial tension, we must conduct separate SCFT calculations of the excess free energy Φ^{m} of an isolated spherical micelle, and of the interfacial tension γ of a flat interface. Both types of calculations are carried out in the grand canonical ensemble, using equal chemical potentials. In the micelle simulation, use of the grand canonical ensemble allows the micelle to automatically adjust its size, composition, and structure so as to minimize the micelle free energy Φ^{m}.

To locate the cmc and γ_{cmc}, a series of calculations of Φ^{m} must be carried out for each system at increasing values of μ_{C}. For each value of μ_{C}, the values of μ_{A} and μ_{B} are chosen from the Flory−Huggins theory, which is the homogeneous limit of SCFT, so as to satisfy conditions for macroscopic phase coexistence, with a pressure $P = 0$ in both A- and B-rich phases. In this series of calculations, the composition of the A-rich phase follows the line $a-b$ in Figure 1 until the cmc is reached. Above the cmc, the Flory−Huggins predictions of the composition of the A-rich phase corresponds to that of the micelle-free matrix within that phase, which differs from the true macroscopic composition when micelles are present.

Solution of the SCF equations for either a spherical micelle or a flat interface requires the numerical solution of a one-dimensional modified diffusion equation. This is obtained using a finite-difference discretization of the radial coordinate in the micelle simulations and of the coordinate normal to the interface in the simulations of a flat interface, as in ref 12.

The excess free energy Φ^{m} of a micelle in a spherical simulation cell of total volume V is given by $\Phi^{\mathrm{m}} = \Phi + P_{\mathrm{I}}V$, where P_{I} is the pressure in the matrix far from the micelle. The predicted number density ρ_{m} of micelles at each value of μ_{C} may be calculated from eq 3, in which we use a standard state concentration $\rho_{\mathrm{m}}{}^0 = 1/(\upsilon N_C M_{\mathrm{C}})$. Values for the critical micelle concentration are obtained from eq 6.

Figures 2−4, which were presented above as schematic plots, were actually generated from the results of a series of SCFT calculations of both Φ^{m} and γ at increasing values of μ_{C} for a system with $f_{\mathrm{A}} = 0.635$, $f_{\mathrm{B}}\chi N_{\mathrm{C}} = 10$, and $N_{\mathrm{A}} = N_{\mathrm{B}} = 100$, for which $\phi_{\mathrm{C}}^{\mathrm{cmc}} = 0.0051$. The change at the cmc in the derivatives of μ_{C} and ϕ_{C}^{f} with respect to total copolymer volume fraction is continuous, but appears quite sharp, and gives an apparent cmc that agrees well with that obtained from eq 6.

4. Results. Micelle Simulations

Figures 5 and 6 compare predictions for the micelle core radius and the cmc, respectively, for both a ternary two-phase system and for a corresponding binary mixture with no B homopolymer. In both figures, the results are shown for systems with symmetric homopolymers, with $N_{\mathrm{A}} = N_{\mathrm{B}}$ and $b_{\mathrm{A}} = b_{\mathrm{B}}$, a fixed length $N_{\mathrm{CB}} = f_{\mathrm{B}}N_{\mathrm{C}}$ for the core block of the copolymer, using three different values of the product $\chi N_{\mathrm{CB}} = 8, 10, 12$. Each line in either figure corresponds to a series of copolymers with equal core block lengths and varying corona block lengths, with $f_{\mathrm{A}} > {}^1\!/_2$ so that micelles form in the A-rich phase.

Figure 5 shows the extent of swelling by comparing core radii of micelles at the cmc of the ternary two-phase system (point b in Figure 1) to those of "dry" micelles at the cmc of the corresponding binary system (point c in Figure 1). Here the micelle core radius is taken to be the radius R of a sphere that contains a volume $4\pi R^3/3 = [f_{\mathrm{B}}N_{\mathrm{C}}M_{\mathrm{C}} + N_{\mathrm{B}}M_{\mathrm{B}}]\upsilon$, which is the

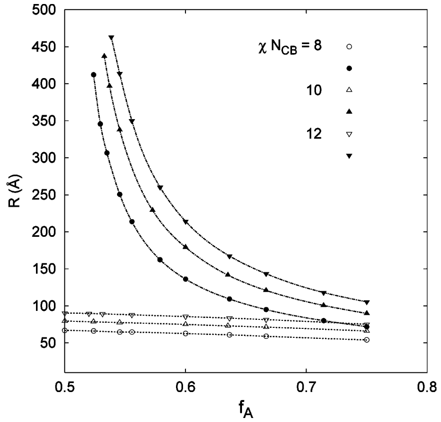

Figure 5. Micelle core radius at the cmc for the ternary two-phase system and binary system considered in Figure 6, vs volume fraction f_A of the corona block. The hollow and solid symbols represent the radii of unswollen and swollen micelles, respectively.

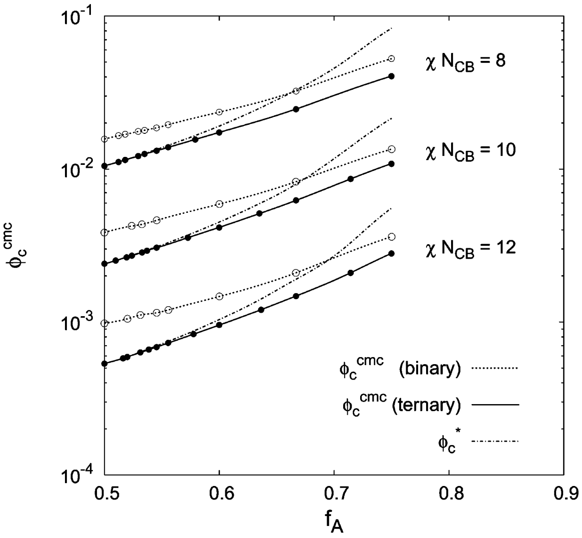

Figure 6. Copolymer volume fraction ϕ_C^{cmc} at the critical micelle concentration of a two-phase ternary system (solid lines), and of a binary mixture of copolymer C in A (short dashed lines), vs volume fraction f_A of the corona block within the copolymer, for systems with homopolymer sizes $\alpha_A \chi N_C = \alpha_B \chi N_C = 10$, for three values of χN_{CB}. Also shown is the copolymer volume fraction ϕ_C^* (dot dashed line) at which the macroscopic interfacial tension of the two-phase system extrapolates to zero. Note that ϕ_C^* always exceeds ϕ_C^{cmc} of ternary two-phase system, but ϕ_C^* drops below ϕ_C^{cmc} of the corresponding binary system for nearly symmetric copolymers.

sum of the volume $f_B N_C M_C v$ occupied by the B blocks of the excess number M_C of copolymers per micelle, plus the volume $N_B M_B v$ of the M_B emulsified B homopolymers. The core radii have been calculated using typical experimental values of $b_A = b_B = 6$ Å with a monomer reference volume of $v = 135$ Å^3, and $N_A = N_B = 100$. Swelling of the micelles in the ternary two-phase system is not significant for $f_A \gtrsim 0.6$, but the micelle core radius diverges as f_A approaches $^1/_2$.

Figure 6 shows the effect of micelle swelling upon the cmc, by comparing predictions for the copolymer volume fraction at the cmc of the ternary system to that at the cmc of the binary system. The cmc of the ternary two-phase system is always lower than that of the corresponding binary system. This is a result of the freedom of the ternary system to minimize the micelle free energy by emulsifying the B homopolymer so as to minimize the bending energy of the interface. The difference between the cmc in the two-phase system and that in the binary mixture is greatest for symmetric copolymers, where the swelling is largest. The difference between these cmc values is always modest, however, and is always less than a factor of 2 in the systems shown here.

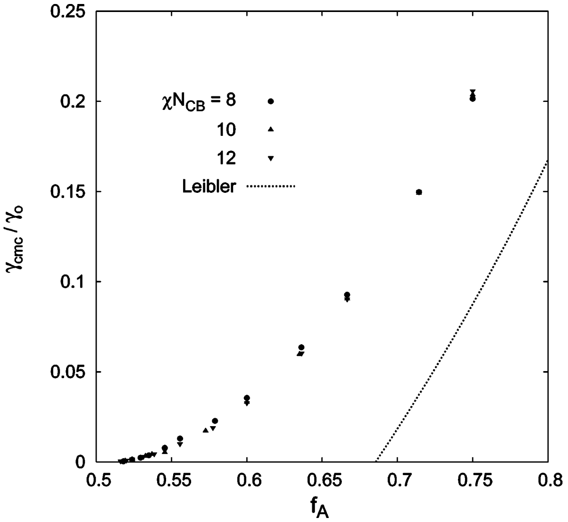

Figure 7. Macroscopic interfacial tension γ_{cmc} at the cmc, normalized by the value γ_0 for a bare interface, vs volume fraction f_A of the copolymer corona block, for the same parameters as those used in Figure 6. Leibler's prediction based on the unswollen micelle is shown with a dotted line for comparison.

This modest difference between the cmc's of swollen and unswollen micelles has a profound effect on the predictions of interfacial tensions. The dotted−dashed lines in Figure 6 show the saturation concentration ϕ_C^* of free copolymer within the A-rich phase at which macroscopic interfacial tension extrapolates to zero (see Figure 4). The predicted value of ϕ_C^{cmc} for a binary system is less than ϕ_C^* for sufficiently asymmetric copolymers, but exceeds ϕ_C^* for f_A near 0.5, in a manner completely consistent with what Leibler found in a more approximate strong-stretching calculation. The values of f_A at which $\phi_C^* = \phi_C^{cmc}$ are actually quite close to the value of $f_A = 0.69$ obtained by Leibler. The cmc of the ternary two-phase system, however, always remains less than or equal to the saturation concentration ϕ_C^*. This implies that the interfacial tension will saturate to a nonzero value above the cmc. Leibler's prediction of a wide range of values of f_A for which $\phi_C^{cmc} > \phi_C^*$ is clearly an artifact of his use of a two-component model for the micelles. The apparent convergence of $\phi_C{}^{cmc}$ and ϕ_C^* at $f_A = {}^1/_2$ is consistent with the prediction of the Helfrich theory that γ should vanish at the cmc for balanced systems.

In Figure 7, we show the SCFT predictions of macroscopic interfacial tension γ_{cmc} above the cmc for the same set of systems as those considered in the two previous figures. As predicted by eq 21, the interfacial tension converges to zero at a balance point $f_A = f_A^{bal} = {}^1/_2$, and exhibits a parabolic dependence on f_A. For comparison, Leibler's prediction is shown as a dotted line. Values of the ratio γ_{cmc}/γ_0, where γ_0 is the bare interfacial tension of the binary A−B mixture, are surprisingly insensitive to the value of χN_C.

The value of copolymer composition f_A^{bal} at which $\tau = 0$ is affected by the choice of homopolymers. Figure 8 again shows the interfacial tension vs f_A, but for the systems with asymmetric homopolymers ($\beta \neq 1$). In each case, there is one value of f_A for which the interfacial tension extrapolates to zero, which in each case corresponds to the value f_A^{bal} at which $\tau = 0$.

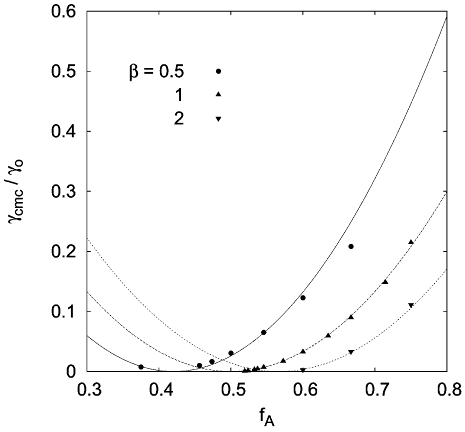

Figure 8. Macroscopic interfacial tension $\gamma_{\rm cmc}$ at the cmc, normalized by the bare tension γ_0, vs copolymer corona volume fraction $f_{\rm A}$ for systems with $f_{\rm B}\chi N_{\rm C} = 10$ with varing values of the ratio $\beta = N_{\rm A}/N_{\rm B}$ of the homopolymer lengths. The solid lines are the predictions of eq 21.

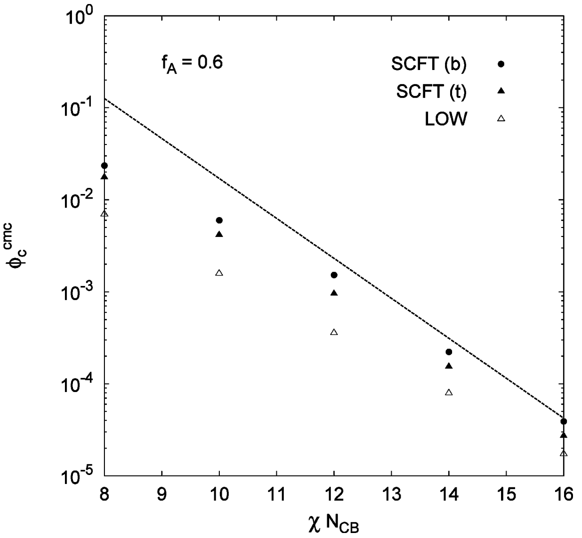

Figure 9. Dependence of the critical micelle concentration $\phi_{\rm C}^{\rm cmc}$ on $\chi N_{\rm BC} = f_{\rm B}\chi N_{\rm C}$ for systems with $f_{\rm A} = 0.6$ and $\alpha_{\rm A}\chi N_{\rm C} = \alpha_{\rm B}\chi N_{\rm C} = 10$. Symbols show predictions for the ternary two-phase system by SCFT (filled triangles) and predictions for a binary system by SCFT (filled circles) and by the approximate strong stretching LOW theory (open triangles). The dashed line is a simple exponential function $Ce^{-\chi N_{\rm BC}}$, with $C = 376$.

Figures 9 and 10 both compare our numerical SCFT predictions of the cmc's of corresponding binary and ternary two-phase mixtures to the predictions for binary mixtures of the analytic models of Leibler, Orland, and Wheeler (LOW)[5] and of Leibler.[11] The LOW theory is based on a simple strong stretching calculation of the free energy of a copolymer micelle in the A homopolymer matrix, in which the density profiles are assumed to be uniform in the core and corona, but some penetration of homopolymer into the core and corona is allowed. The theory denoted "Leibler" is further simplified by neglecting both homopolymer penetration of the corona (thus assuming a dry brush) and micelle translational entropy.[11]

In both binary or ternary systems, the cmc exhibits a roughly exponential dependence $\phi_{\rm C}^{\rm cmc} \propto e^{-\chi N_{\rm CB}}$ on the product $\chi N_{\rm CB}$, and a much weaker dependence on the length $N_{\rm CA}$ of the corona block. Both analytic theories capture the dominant exponential dependence of the cmc on $\chi N_{\rm CB}$, shown in Figure 9, but they predict values somewhat lower than those obtained from numerical SCFT. Both analytic theories predict too weak a dependence on $f_{\rm A}$, as shown in Figure 10.

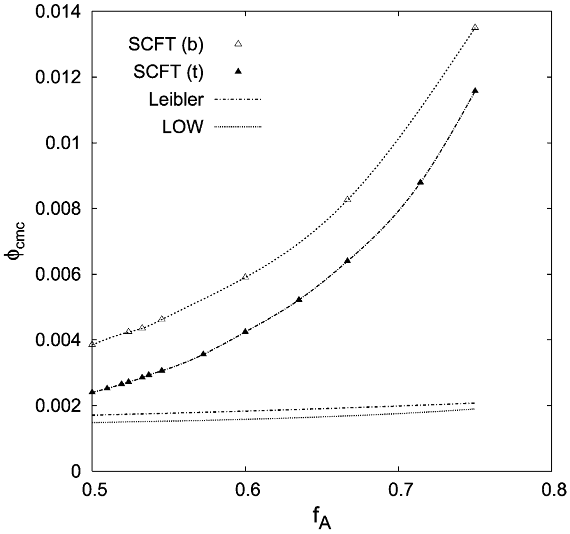

Figure 10. Comparison of SCFT predictions for the cmc $\phi_{\rm C}^{\rm cmc}$ of a ternary two-phase system (filled triangles) and a binary system (open triangles) to the strong stretching predictions for the binary system by Leibler (dot dashed line) and LOW (dotted line) for the system of $\chi N_{\rm CB} = 10$ among the cases considered in Figure 6.

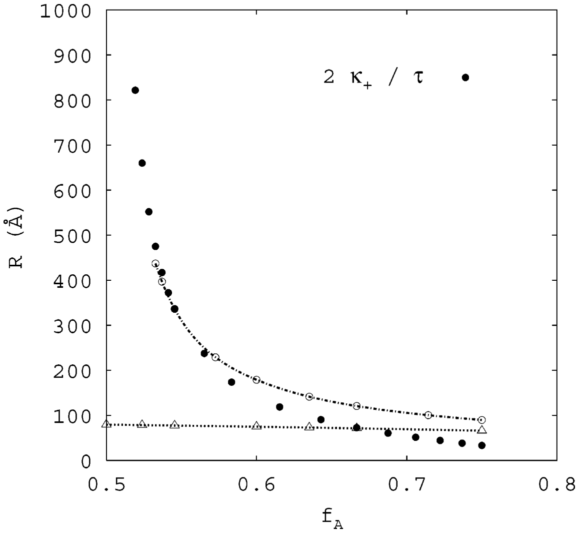

Figure 11. Comparison of micelle core radii obtained from direct micelle simulations (hollow circles) and from Helfrich bending elasticity (solid circles) as a function of $f_{\rm A}$. They are consistent for $f_{\rm A} \lesssim 0.58$ but the latter starts to underestimate the radii for larger $f_{\rm A}$. Radii of "unswollen" micelles in a binary mixture with no B homopolymer are shown as open triangles.

5. Results. Helfrich Theory

The structure and free energies of very highly swollen micelles are best understood in terms of the Helfrich theory. Numerical predictions can be obtained for $f_{\rm A}$ near $f_{\rm A}^{\rm bal}$, where direct simulation of highly swollen micelles becomes difficult, by combining analytic predictions of the Helfrich theory with numerical SCFT calculations of the elastic parameters κ_+ and τ. Our calculations of the Helfrich elastic parameters are discussed in a separate paper.[12] Figures 11 and 12 compare predictions obtained from numerical SCFT simulations of entire micelles (as discussed above) to more approximate predictions obtained by using numerically calculated values of the elastic parameters in the Helfrich theory. Both figures show data for system with $\chi N_{\rm CB} = 10$, with all other parameters identical to those used in Figures 5−7.

Figure 11 compares values of the core radius R obtained from SCFT simulations of micelles to the values $R = 2\kappa_+/\tau$ predicted

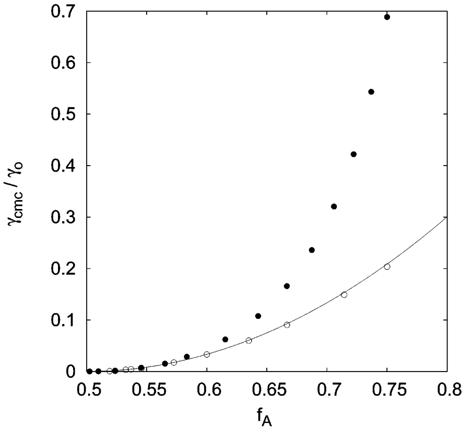

Figure 12. Predictions of $\gamma_{\mathrm{cmc}}/\gamma_0$ from direct micelle simulations (hollow circles) and from the Helfrich theory, using eq 20 (solid circles) vs f_A. They are consistent for $f_A \lesssim 0.6$ but start to deviate for larger f_A. The solid line is the simple quadratic approximation given in eq 21 (solid line), with τ' and κ_+ evaluated at $C = 0$, which fits the results of the direct micelle simulations suprisingly accurately.

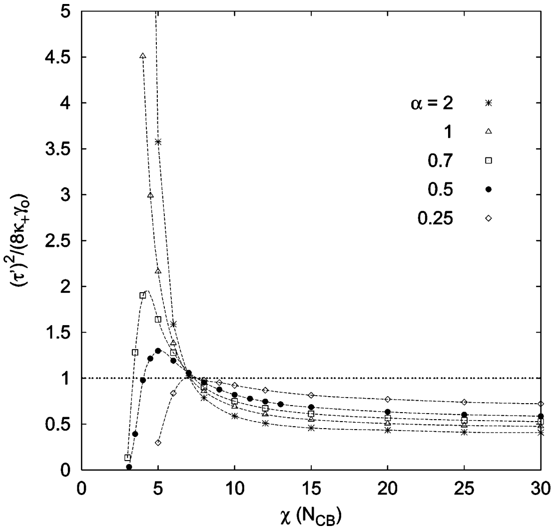

Figure 13. Dimensionless quantity $D/8 \equiv \tau'^2/8\kappa_+\gamma_o$ as a function of χN_{CB} for several values of α. For $D/8 = 1$, the parabolic dependence of γ_{cmc} upon f_A near $f_A = {}^1/_2$ would extrapolate to γ_0 for $f_A = 1$.

by the Helfrich theory. The core radii reported for the full micelle simulations have been calculated as described in Figure 5. The radius predicted by the Helfrich theory corresponds to that of the Gibbs dividing surface which is used to calculate κ_+ and τ for each value of f_A and for which there is no interfacial excess concentration of A or B monomers.

The predictions of the Helfrich theory for R agree well with the results of full micelle simulations for nearly symmetric copolymers, with $f_A \lesssim 0.58$, for which the micelle radius significantly exceeds that of an unswollen micelle (also shown). For copolymers with $f_A \gtrsim 0.60$, however, for which the micelle radius in the ternary system is similar to that obtained in the absence of the B homopolymer, the Helfrich theory predicts too small a radius. The Helfrich theory thus appears to be accurate over a surprisingly wide range of equilibrium micelle radii, extending almost down to that of a dry micelle, but only a limited range of values of f_A.

Figure 12 tests the validity of the Helfrich theory predictions for the ratio $\gamma_{\mathrm{cmc}}/\gamma_0$. Results of the full micelle simulations described in the previous section (open circles) have been compared to two more approximate expressions: The closed circles are obtained from eq 20, using the same values of $\kappa(f_A)$ and $\tau(f_A)$ as those used in Figure 11, while the solid line is the prediction of eq 21, which has been constructed values of τ' and κ_+ evaluated at $f_A^{\mathrm{bal}} = {}^1/_2$. Equation 20 agrees reasonably well with the full SCFT results only for $f_A \lesssim 0.6$. This is similar to the accuracy found in the analogous predictions of the core radius. Remarkably, however, the simple quadratic expression of eq 21 is in nearly perfect agreement with the full simulations over the full range of $f_A = 0.5-0.75$ explored here. This excellent agreement can also be observed in Figure 8 for asymmetric systems with $N_A \neq N_B$.

Equation 21 implies that the dependence of $\gamma_{\mathrm{cmc}}/\gamma_0$ on f_A near $f_A^{\mathrm{bal}} = {}^1/_2$ for systems with symmetric homopolymers can be approximated by a harmonic function ${}^1/_2 D(f_A - f_A^{\mathrm{bal}})^2$, with a single dimensionless prefactor

$$D = (\tau')^2/(\kappa_+\gamma_0) \tag{22}$$

in which all of the variables are evaluated in a symmetric reference state with $f_A = {}^1/_2$. The dependence of this prefactor upon the product χN_{CB} for the several values of $\alpha = N_A/N_C$ in this reference state is shown in Figure 13. For values of $\alpha < 1$, for which there exists a stable Lifshitz point, the quantity D approaches zero continuously as χN_{CB} approaches its value at the Lifshitz point, $(\chi N_{\mathrm{CB}})_L = (1 + 2\alpha^2)/\alpha$.[29] For $\alpha = 1$, which is the value at which the Lifshitz point is first preempted by a tricritical point, D presumably appears to diverge at the Lifshitz point. The divergence appears because, at $\alpha = 1$, κ_+ approaches zero (Figure 4 in ref 12) at the Lifshitz point, but τ' appears not to, and instead appears to approach a constant for $\alpha = 1$ and to diverge for $\alpha > 1$ (Figure 10 in ref 12) At high values of χN_{CB}, far from the Lifshitz point, the value of D becomes rather insensitive to changes in χN_{CB}, consistent with the behavior noted in Figure 7.

6. Other Possible Phenomena

Thus far, we have considered only the possibility of the formation of swollen spherical micelles and its relation to interfacial tension in ternary two-phase systems. There are, however, several possible competing alternatives in the systems of interest here.

6.1. Cylindrical Micelles. It is possible for block copolymers in dilute solutions to form cylindrical, rather than spherical, micelles. In binary systems of A homopolymer and AB copolymer, analytic strong stretching calculations by Mayes and de la Cruz[23] and numerical SCFT calculations by Matsen[20] and by Janert and Schick[34] have predicted the formation of either cylindrical micelles[23] or highly swollen periodic hexagonal mesophases[20,34] in some systems of symmetric and slightly asymmetric copolymers.

In an analysis of the behavior of highly swollen micelles in ternary systems, which was based upon the Helfrich theory of weakly curved saturated interfaces, Safran and Turkevich[35] found that spherical micelles are always preferred over cylinders along the emulsification failure line in systems in which $\bar{\kappa} < 0$, as found here by SCFT. Systems with $\bar{\kappa} > 0$ would be unstable to the formation of multiply connected surfaces of constant mean curvature. In this theory, a transition from spherical to cylindrical micelles can, however, be induced in a single-phase micellar solution by decreasing the volume fraction of the B homopolymer. The preference for spherical micelles along the emulsification line is a result of the existence of a negative Gaussian rigidity $\bar{\kappa} < 0$, which favors the formation of spherical over cylindrical surfaces. Along the emulsification failure line, both spherical and cylindrical micelles can freely adjust their radii by transferring molecules from the coexisting excess phase, and, in a system with a negative Gaussian rigidity, the free energy per unit area for a spherical micelle is always less than that for a cylindrical micelle with the same mean curvature C.

The Helfrich theory is valid only for systems containing monolayers with low spontaneous curvatures, which tend to form highly swollen micelles near the emulsification failure line. In the opposite limit of highly asymmetric copolymers, however, we also expect spherical micelles to be favored over cylindrical micelles, as a result of packing constraints. These considerations suggest that spherical micelles will always be preferred over cylindrical micelles in the micellar phase of a two-phase system.

The above considerations also suggest that addition of the B homopolymer to a binary system that forms cylindrical micelles must generally cause a transition from cylindrical to spherical micelles somewhere along the line of critical micelle concentrations that extends from the binary system to the emulsification failure line. We have not systematically pursued this idea. As an example, however, we have compared the cmc's for spherical and infinite cylindrical micelles in a single-phase binary system with $\chi f_B N_C = 10$ and $\alpha_A = {}^1/_2$ over a same range of f_A, for which we find that spherical micelles are narrowly preferred over cylinders even in the absence of the B homopolymer. Cylindrical micelles would presumably be more favorable for symmetric copolymers with larger values of χN_{CB} or α, for which the corona block would be less strongly swollen by homopolymer.[23]

6.2. Lamellar Phases. The model of noninteracting spherical micelles discussed above predicts an infinite micelle radius in a system with symmetric copolymer and homopolymers. This prediction is obtained only because we have neglected excluded volume interactions between swollen micelles, which are assumed to remain irrelevant even as the predicted micelle radii diverge. In reality, systems with balanced surfactants are expected to form either a lamellar phase or a bicontinuous microemulsion.

Monolayers of symmetric block copolymers with molecular weights less than that of either homopolymer are known to exhibit a weak entropic attraction when separated by distances for which opposing copolymer brushes slightly overlap. This attraction can prevent swelling of the lamellar spacing, and lead, in a ternary system, to regions of three-phase coexistence of a copolymer-rich lamellar phase with two excess phases of essentially pure A and B homopolymer.[28] Thompson and Matsen[22] have used numerical SCFT to study the effective interaction between symmetric monolayers within a ternary lamellar phase, and identified a line of values of α as a function of χN_C at which the interaction between monolayers changes from effectively repulsive (at lower α) to attractive (at higher α). This apparent critical value of α decreases very slowly with increasing χN_C, varying from $\alpha \simeq 1.3$ near the critical point to $\alpha \simeq 0.8$ at $\chi N_C > 100$. Symmetric systems with $\alpha < 0.8$ are, however, not expected to form a collapsed lamellar phase. The attraction between brushes that can cause the collapse of a lamellar phase could presumably also cause two-phase coexistence between ordered dense crystals of spherical or cylindrical micelles, but the interactions between spheres and cylinders have not been as carefully studied.

When the interactions between monolayers in a lamellar phase are repulsive, SCFT predicts that the lamellar spacing d may be increased with decreasing surfactant concentration until d diverges at an unbinding transition. The predicted unbinding transition in a system with balanced copolymer monolayers occurs at a copolymer concentration corresponding to the chemical potential $\mu_C^*(T)$ of a saturated monolayer, at which the interfacial excess free energy per area γ vanishes.

6.3. Bicontinuous Microemulsions. Systems of balanced copolymers for which SCFT predicts a lamellar phase with an unbinding transition have been observed to form a transition to a bicontinuous microemulsion phases near the predicted unbinding transition. Bicontinuous microemulsion phases have been observed to be stable in symmetric ternary mixtures over a narrow range of copolymer concentrations near the predicted unbinding transition, and to exhibit three-phase coexistence with excess phases of the A and B homopolymer.[15] By analogy to the behavior observed in small molecule mixtures, the bicontinuous microemulsion phase is expected to be stable only for systems with a limited range of values of f_A near f_A^{bal}. The most important limitation of the theory of droplet microemulsions presented in this paper is that the region near the balance point in which the Helfrich theory is valid, and in which the droplet microemulsion model predicts a very small macroscopic interfacial tension, is precisely that in which one expects to find either a collapsed lamellar phase or a bicontinuous microemulsion phase rather than a droplet microemulsion.

R. Strey has presented an analysis of the three-phase state in which a bicontinuous microemulsion phase coexists with excess oil and water phases. His analysis is closely analogous to that given for a droplet microemulsion given in section 2.5, and captures some important aspects of the observed behavior of the interfacial tension in systems that contain a bicontinuous microemulsion.[24] Here we present a variant of Strey's analysis, using a grand canonical formulation analogous to that used in section 2.5, and discuss its predictions, limitations, and relationship to experimental observations.

We consider an idealization of the interfacial surface in a bicontinuous microemulsion phase as a multiply connected surface with a characteristic structural length ξ, a constant mean curvature C, and an average Gaussian curvature $\langle K\rangle \propto 1/\xi^2$. This surface divides internal space into two interpenetrating domains rich in oil and water, or rich in the A and B homopolymers. When a microemulsion coexists with two homogeneous phases, the local pressure within either of the interpenetrating domains must be equal to the macroscopic pressure P in either excess phase. If we take $P = 0$ for mathematical convenience, the grand canonical free energy Φ of a bicontinuous microemulsion phase becomes equal to the excess free energy $\Phi + PV$ of the interfacial surface. The free energy of a microemulsion phase can thus be approximated by a surface integral

$$\Phi = -A\Gamma^*\delta\mu + \int \mathrm{d}A \left\{\frac{1}{2}\kappa C^2 - \tau C + \bar{\kappa}K\right\} \qquad (23)$$

of the Helfrich expression for the interfacial tension $\gamma(T,\delta\mu, C, K)$, in which A is the total interfacial area and $\int \mathrm{d}A$ is integral over this area. The Gauss−Bonnet theorem states that the integral $\int \mathrm{d}A\ K$ depends only upon the topology of the structure.[33] Minimizing the bending energy for a structure of fixed topology yields a surface of constant (i.e., homogeneous) mean curvature $C = \tau/\kappa$. For such a surface, the free energy per unit area is

$$\frac{\Phi}{A} = -\Gamma^*\delta\mu - \frac{1}{2}\kappa C^2 + \bar{\kappa}\langle K\rangle \qquad (24)$$

Here, $\langle K\rangle = A^{-1}\int \mathrm{d}A\ K$ is the areal average of the Gaussian curvature, which is negative for any multiply connected surface.

The condition for phase coexistence at $P = 0$ is that $\Phi/V = 0$. This implies that

$$-\Gamma^*\delta\mu = \frac{1}{2}\kappa C^2 - \bar{\kappa}\langle K\rangle \tag{25}$$

for a microemulsion in three-phase coexistence. Using eq 25 for $\delta\mu$, we find that the interfacial tension of any flat macroscopic monolayer, with $C = \langle K\rangle = 0$, in a three-phase system that contains such a microemulsion is

$$\gamma = \frac{1}{2}\kappa C^2 - \bar{\kappa}\langle K\rangle \tag{26}$$

This relation is slightly different from Strey's final result (his eq 15),[24] because he used the relation $C = \tau/\kappa_+$ appropriate to a spherical surface (his eq 8), rather than setting $C = \tau/\kappa$. In either variant, however, the relation is quite similar to eq 19 for the interfacial tension of a droplet microemulsion, and it exhibits a similar quadratic dependence on the spontaneous curvature $C \propto \tau$. In the case of a multiply connected surface, however, γ extrapolates to a nonzero minimum value $\gamma_{\text{min}} = -\bar{\kappa}\ \langle K\rangle$ at the balance point, which is positive only if $\bar{\kappa} > 0$.

In the systems studied by Strey and co-workers, it is possible to measure separately the interfacial tension γ_{ab} of the macroscopic interface between oil (a) and water (b) phases, the tension γ_{ac} between the oil and microemulsion (c) phase, and the tension γ_{bc} between the water and microemulsion phases in a three-phase system. γ_{ac} and γ_{bc} approach zero continuously at the upper and lower end critical temperatures, T_{u} and T_{l}, respectively. In these systems, the oil−water ab interfacial tension generally satisfies the inequality $\gamma_{\text{ab}} < \gamma_{\text{ac}} + \gamma_{\text{bc}}$, so that the microemulsion phase does not wet the interface between oil and water. The ab interface is thus believed to consist of a single monolayer of surfactant. Equation 26 thus provides a prediction for the interfacial tension γ_{ab} of this monolayer interface in a nonwetting three-phase state. A scenario for polymer mixtures analogous to that found by Strey and co-workers in these small molecule mixtures is shown schematically in Figure 14.

The measured interfacial tension γ_{ab} in these systems is well described by a quadratic function $\gamma_{\text{ab}} = \gamma_{\text{min}} + \text{B}(T - T_{\text{m}})^2$. This is the form suggested by the above argument for systems in which $C \propto T - T_{\text{m}}$ near the balance point. Strey and co-workers have used Strey's model to extract positive values of $\bar{\kappa}$ from their interfacial tension data, by using the relationship $\gamma_{\text{min}} = -\bar{\kappa}\langle K\rangle$ for the minimum interfacial tension and an estimate for the average Gaussian curvature $\langle K\rangle$.

Strey's model provides an appealing explanation for the observed quadratic dependence of γ upon distance from the balance point, based on a generalization of the reasoning used in section 2.5 to describe a droplet microemulsion. Unfortunately, the analysis does not provide a consistent description of the thermodynamics of a bicontinuous microemulsion. In a balanced system, with $\tau = 0$, a model of a microemulsion as a minimal surface, with $C = 0$, predicts an interfacial free energy per area $\Phi/A = \bar{\kappa}\langle K\rangle$, in which $\langle K\rangle$ is a negative number that varies with structural length scale ξ as $-\langle K\rangle \propto 1/\xi^2$. Assuming that $\bar{\kappa}$ is positive yields a free energy for the microemulsion phase lower than that of the lamellar phase, but it also leads to a mechanically unstable structure: When $\bar{\kappa} > 0$ and $\tau = 0$, the minimum possible free energy is obtained in the limit $\xi \rightarrow 0$ of an infinitely dense minimal surface. As a result of this instability, Strey's model cannot predict a value for ξ in the three-phase state, or a value for γ_{min}, without additional experimental input.

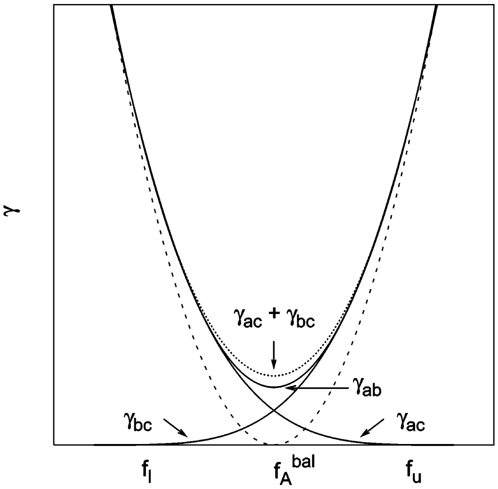

Figure 14. Schematic diagram of the expected variation of interfacial tension with volume fraction f_{A} of the A block through a region of three-phase coexistence near the balance point, constructed by analogy to the behavior observed experimentally in mixtures of oil (a), water (b), and nonionic surfactant (c). The upper and lower end critical values of f_{u} and f_{l}, at which γ_{ac} and γ_{bc} continuously approach zero, correspond to critical end points at which the middle microemulsion phase merges continuously with the a- and b-rich phases, respectively. The interfacial tensions are assumed to obey the inequality $\gamma_{\text{ab}} + \gamma_{\text{bc}} > \gamma_{\text{ab}}$, so that the middle microemulsion phase does not wet the ab interface. The dashed line that yields $\gamma = 0$ at the balance point is the prediction of the theory developed here for spherical micelles.

A consistent description of a bicontinuous microemulsion phase must thus include physics beyond that contained in the Helfrich theory. Two proposals have been made that are consistent with the description of the interface in the microemulsion as a surface of nearly constant mean curvature $C = \tau/\kappa$ that is stabilized by the existence of a positive Gaussian rigidity.[19] One is (like the Helfrich model) an essentially mechanical model, while the other explicitly takes into account of the free energy arising from interfacial fluctuations. The mechanical model, due to Wennerstrom, Olsson, and co-workers,[30−32] generalizes the Helfrich model by including terms higher than second order in the Taylor expansion of the interfacial free energy density as a function of curvature. In this model, the length ξ is determined by a balance between a positive $\bar{\kappa}$, which favors the formation of a multiply connected surface, and anharmonic terms that prevents the structure from collapsing. In the fluctuation theory, the effects of interfacial fluctuations are absorbed into renormalizations of the elastic parameters κ, $\bar{\kappa}$, and τ of the Helfrich theory, yielding renormalized values that are found to vary logarithmically with increasing structural length ξ.[13,17,33] In particular, the renormalized Gaussian rigidity $\bar{\kappa}$ is found to increase with increasing ξ, or decreasing surfactant concentration. The fluctuation model predicts coexistence of a balanced bicontinuous structure with an excess homogeneous phase (in the original discussions of binary surfactant/solvent mixtures by Golubovic[25] and by Morse[26]) or two homogeneous phases (in a straightforward extension to balanced ternary mixture) at a surfactant concentration for which $\bar{\kappa}_{\text{R}}$ has a small positive value $\bar{\kappa}_{\text{R}} \sim kT$.

Sottmann and Strey[27] have compared interfacial tension data of different model surfactant mixtures, and found that the minimum interfacial tension obtained for many different surfactants varies with the structural length scale ξ of the balanced middle-phase microemulsion as $\gamma_{\text{min}} = AkT/\xi^2$, where A is an apparently universal dimensionless prefactor. If interpreted as a purely mechanical phenomena, using Strey's analysis, this would suggest a universal positive value of $\bar{\kappa}$ of order kT for all of these systems. This observation appears to be most consistent with the idea that $\gamma_{\min}$ is instead related to a renormalized Gaussian rigidity $\bar{\kappa}(\xi)$, which is predicted by the fluctuation model to always be a positive quantity of order kT within a middle phase microemulsion. This idea will be fleshed out elsewhere.

7. Conclusion

We have combined numerical SCFT with the Helfrich theory to describe two-phase systems in which an A-rich phase of swollen B in A spherical micelles coexists with a homogeneous B-rich phase and to calculate the interfacial tension between these phases. In the limit of nearly balanced surfactants, in which micelle cores swell significantly by emulsifying the B homopolymer, SCFT results agree well with the Helfrich theory. The macroscopic interfacial tension is found to vary quadratically with the monolayer spontaneous curvature, and extrapolates to zero at a balance point. Numerical SCFT was found to yield a simple parabolic dependence of γ on distance from the balance point even outside the limited range of parameters in which the underlying Helfrich theory is valid. The value of the ratio $\gamma_{\rm cmc}/\gamma_0$ of the interfacial tension above the cmc to the bare interfacial tension is surprisingly insensitive to changes in $\chi N_{\rm C}$, except near the Lifshitz point. Both the results of experiments on mixtures of oil, water, and nonionic surfactant and an analysis by Strey suggest that a similar parabolic dependence should extend into the three-phase coexistence region near the balance point, in which a bicontinuous microemulsion phase coexists with two excess phases.

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