Competitive Adsorption of Amphiphilic Molecules and the Stability of Water-Swollen Micelles in Oil

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Motivated by recent attempts to confine biochemical processes inside water-in-oil microemulsions, we studied the composition and stability of mixed-amphiphile water-swollen micelles in oil from a theoretical point of view. A novel adsorption model demonstrates how the micellar contents (DNA, proteins, etc.) can dramatically affect the composition of the amphiphilic film and the resulting distribution of micelles. Special attention is given to the effect of electrostatic interactions within the micelles as well as between different ones. Since in a low dielectric medium charge fluctuations can lead to long-range intermicellar attractions, we suggest that the presence of amphiphilic polymers in the surfactant film may be needed to stabilize such micromolecular systems.

I. Introduction

Recently, several groups have used microemulsions (swollen micelles) as nanocontainers for isolating and analyzing biochemical processes.1–3 The advantage of this method is that a very large number of micelles can include all the ingredients needed for the various biochemical stages of the reactions, while the surrounding medium (oil) is biochemically inert and effectively isolates each micelle. One of the possible applications of such a process (termed in vitro compartmentalization) is the development of specialized enzymes (or other proteins) by testing a large number of mutations in parallel.3

For the biochemical compartmentalization to be effective, it is important to ensure that different micelles do not exchange contents with each other; otherwise, the link between the gene that encodes a mutant enzyme (genotype) and the enzyme’s functional trait (phenotype) is lost. The main mechanism of material exchange is through intermicellar collisions.4 Since the collision rate depends strongly on the intermicellar interactions, it is important to understand and control these interactions. It is also advantageous to control the interactions between the micellar contents and the interfacial layer. For example, keeping the biochemical ingredients away from the proximity of the water/oil interface by means of repulsive interactions further reduces the exchange rate between different micelles since it adds a kinetic barrier for the exchange process.

One can also think of situations where the reactions that take place within the micelles must occur at the micellar surface. This can again be achieved by appropriately tuning the surface composition. One example are experiments aimed at understanding the coupling of various proteins with the cell membrane (see, e.g., ref 5).

From all this it is clear that such experiments must address two issues in parallel: (i) localization of the contents (e.g., DNA and enzymes) within the micelles and (ii) intermicellar stability. Both processes strongly depend on the composition of the water/oil interface. Although previous studies have looked in detail at the structure of inverted micelles with different contents,6–11 the influence of the micellar content on the composition of the interfacial layer has not been studied yet.

Allowing the interfacial composition to vary introduces an additional degree of freedom to the system and the result is essentially a five component system consisting of water, oil, two types of amphiphilic molecules, and macromolecules that model the reactive contents of the micelle. We address the complexity of the system by introducing in section 2 a simple model that predicts the interplay between the micellar content and the interface composition in a mixture of two different amphiphilic molecules. We show that strong repulsion (attraction) between the micellar contents and one amphiphilic species leads to preferential adsorption of the interacting species onto empty (filled) micelles. For example, in the regime where the system is dominated by strong contents—amphiphile repulsion (attraction), the amphiphiles adsorb first only to the empty (filled) micelles and do not adsorb onto the filled (empty) micelles until the empty (filled) micelles are fully saturated with amphiphiles. In the regime where amphiphile—amphiphile repulsions compete with amphiphile—contents interactions we find that the adsorption process occurs in three distinct stages as a function of

that takes place inside the micelle. For example, if the activity of the process decreases when one of the ingredients, such as a DNA molecule, adsorbs onto the interfacial layer, one can compensate for this by adding to the interfacial layer an amphiphile (e.g., negatively charged surfactants or polymer chains) that repels the DNA molecule from the interface. In other cases, adsorption might be actually preferable, in which case an attractive amphiphile can be introduced.

The composition of the interfacial layer also affects intermicellar interactions, which determine the stability of micelles against collisions. Since in some experiments, the purpose of using microemulsions is to explore a large number of possibilities in parallel, it is important to keep the ingredients from transferring between micelles. Amphiphilic copolymers, for example, can keep the micelles well isolated from each other (the details of these interactions will be described in the appendix).

The biochemical activity is maintained by the presence of various macromolecules inside the micelles. For simplicity, we restrict ourselves to the case where the micelle includes a single polymer or macroion, which represents a DNA molecule, globular proteins, etc. Since not all micelles are necessarily biochemically active, we assume that only a fraction, $x_p$, of the micelles are filled with the polymer (or macroion) while a fraction, $1 - x_p$, remains empty. The fraction of filled micelles, $x_p$, is determined by the number of macroions in the system. We further assume that only the additional amphiphiles (whether ionic surfactants or amphiphilic polymers) interact strongly with the micelle interior. Ionic surfactants interact with a charged polymer or macroion through electrostatic interactions, while amphiphilic polymers interact with the micelle interior via steric interactions of the hydrophilic tail, arising from the entropic restriction of excluded volume. Similar interactions are also present among the additional amphiphiles: ionic surfactants carrying similar charges repel each other electrostatically while amphilic polymers exhibit steric repulsions. The explicit details of these interactions are discussed below in section 3.

In this section, we use a phenomenological model, appropriate to either steric or electrostatic interactions, to predict the repartitioning of the interacting amphiphilic molecules (referred to hereafter as amphiphiles) and the noninteracting surfactant molecules (termed surfactants) between the filled and empty micelles. We show that depending on the strength of the amphiphile—contents and amphiphile—amphiphile interactions some or all of the following adsorption stages occur: (I) adsorption only to the empty (filled) micelles, (II) adsorption to both empty and filled micelles, and (III) adsorption only to the filled (empty) micelles.

The free energy of the micelles has contributions from both filled micelles and the empty ones. The free energy per amphiphilic molecule of the filled micelles can be written as

$$F_p = x_p f_p \ln f_p + (1 - f_p) \ln(1 - f_p) + \varepsilon_p + \frac{\sigma_p^2}{2 f_p} \tag{1}$$

where $f_p$ is the fraction of amphiphiles in the filled micelles. Here and in the following all energies are expressed in units of the thermal energy $k_B T$. The first two terms in eq 1 represent the translational entropy of the amphiphiles.

**Figure 1.** Schematic view of mixed-amphiphiles, water-in-oil micelles. The composition of the amphiphilic layer at the water/oil interface can consist of (top) two different surfactant species or (bottom) a mixture of surfactant molecules (not shown) and long amphiphilic diblock copolymers.

amphiphile concentration. At first, the interacting amphiphiles adsorb only to the empty (filled) micelles, while in the second stage adsorption continues concurrently to both empty and filled micelles. Finally, once the empty (filled) micelles are saturated with amphiphiles, adsorption continues only to the filled (empty) micelles. If the interactions are comparable to the thermal energy, entropy also plays a role and the distinction between the different adsorption stages is smoothed out.

To make contact with the experimental systems, we provide in section 3 simple estimates for the interaction parameters between in two cases: (i) a mixture of charged and neutral surfactant in the presence of salt within the micelles, so that intramolecular interactions are dominated by screened electrostatic interactions of the Debye–Hückel type; (ii) a mixture of small surfactant molecules and long amphiphilic diblock copolymers, where the interactions of the copolymer chains are dominated by steric (excluded volume) interactions. Finally, in section 4, we summarize our main conclusions, discuss some possible extensions of the model, and suggest future experimental directions that could test our predictions. To complement our work, we summarize in the Appendix the different contributions to intermicellar interactions. It turns out that electrostatic interactions across a low-dielectric medium like oil are attractive and long-range because of the absence of small mobile ions in the medium. In contrast, steric interactions between long hydrophobic chains can stabilize micelles against collisions.

**II. Competitive Adsorption Model**

A schematic picture of water-in-oil micelles is presented in Figure 1. A thin layer of amphiphilic molecules surrounds the water micelles and stabilizes the system against macrophase separation. Typically, the interfacial layer consists of surfactant molecules with a hydrophilic headgroup and a hydrophobic tail. Other possibilities include long chain, amphiphilic polymers where a hydrophobic chain and a hydrophilic chain are chemically attached to each other.

The composition of the interfacial layer can be modified in order to improve the quality or efficiency of the process.

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In this section, we use a phenomenological model, appropriate to either steric or electrostatic interactions, to predict the repartitioning of the interacting amphiphilic molecules (referred to hereafter as amphiphiles) and the noninteracting surfactant molecules (termed surfactants) between the filled and empty micelles. We show that depending on the strength of the amphiphile—contents and amphiphile—amphiphile interactions some or all of the following adsorption stages occur: (I) adsorption only to the empty (filled) micelles, (II) adsorption to both empty and filled micelles, and (III) adsorption only to the filled (empty) micelles.

The free energy of the micelles has contributions from both filled micelles and the empty ones. The free energy per amphiphilic molecule of the filled micelles can be written as

$$F_p = x_p f_p \ln f_p + (1 - f_p) \ln(1 - f_p) + \varepsilon_p + \frac{\sigma_p^2}{2 f_p} \tag{1}$$

where $f_p$ is the fraction of amphiphiles in the filled micelles. Here and in the following all energies are expressed in units of the thermal energy $k_B T$. The first two terms in eq 1 represent the translational entropy of the amphiphiles.
and surfactants on the micellar surface, respectively. The third term accounts for the interaction of the amphiphiles with the macroion, where $\epsilon$ is the interaction energy of one amphiphile with the macroion. Without loss of generality we assume $\epsilon > 0$ (i.e., repulsive). Note that a negative value for $\epsilon$ (i.e., attractive amphiphile–macroion interactions) is equivalent to reversing the role of the empty and filled micelles. Finally, the last term primarily accounts for the repulsion between the amphiphiles. In the electrostatic case, $\sigma$ is due to Coulomb repulsions while in the case of amphiphilic polymers it is due to steric repulsions between the polymer tails. All specific details regarding the amphiphiles and the micellar content are contained in the phenomenological interaction parameters $\epsilon$ and $\sigma$. Some predictions to the values of $\sigma$ and $\epsilon$ are discussed in section 3 below.

The free energy per amphiphile of the empty micelles is

$$ F_0 = (1 - x_p)[f_0 \ln f_0 + (1 - f_0) \ln(1 - f_0) + \sigma \epsilon_0^2] $$

where $f_0$ is the fraction of amphiphiles in the empty micelles. Since the composition of the amphiphilic layer is the main degree of freedom here, only terms that depend on the composition appear explicitly in eqs 1 and 2. Various interactions, including surfactant–surfactant interactions, contribute to these terms and their coefficients can be viewed as effective interaction coefficients. For clarity, we have assumed that the repulsion between the amphiphiles in the empty micelles is the same as in the filled micelles. This is not always necessarily the case. For example, if the radii of the filled micelles are different than those of the empty ones—the interaction parameter, $\sigma$, is likely to be affected (see, e.g., ref 12). Our formalism can be easily generalized to take this effect into account.

For a given fraction, $f$, of amphiphiles in the entire system, the fractions $f_p$ and $f_0$ are related through

$$ x_p f_p + (1 - x_p) f_0 = f $$

or, equivalently,

$$ f_0 = \frac{f - x_p f_p}{1 - x_p} $$

The equilibrium composition of the filled and of the empty micelles can be determined by the condition that $\delta F / \delta f_p = 0$, where $F = F_p + F_0$. An equivalent requirement is that the chemical potential of the amphiphiles be the same in the empty and filled micelles. This condition yields

$$ \ln\left(\frac{f_p}{1 - f_p}\right) + \epsilon + \sigma \epsilon_0 = \ln\left(\frac{f_0}{1 - f_0}\right) + \sigma \epsilon_0 $$

or

$$ f_0 = \frac{f_p}{f_p + (1 - f_p)e^{-\epsilon - \sigma \epsilon_0 + \sigma \epsilon_0}} $$

which is reminiscent of the Frumkin adsorption isotherm and reduces to the Langmuir adsorption isotherm in the limit $\sigma \rightarrow 0$.

The solution to eqs 4 and 5 determines the compositions of the filled and empty micelles. Typical examples are depicted in Figure 2 by solid curves. In part a, $x_p = 0.5$, $\epsilon = 5$, and $\sigma = 10$ while in part b, $x_p = 0.5$, $\epsilon = 4$ and $\sigma = 2$. Since $\sigma > 0$, the energy of an amphiphile is higher in the filled micelles than in the empty ones, and it follows that $f_0$ is always greater than $f_p$. Typically, the adsorption process consists of three stages. (I) At first, the amphiphiles adsorb only to the empty micelles and $f_0 = 0$. Because of the lateral repulsion between the amphiphiles, this stage is followed by a second stage (II) where the amphiphiles adsorb to both empty and filled micelles. (III) Finally, when the empty micelles are saturated with amphiphiles ($f_0 = 1$), adsorption continues only to the filled micelles. A few cases are of particular interest.

(i) If $\epsilon \ll 1$, the empty and filled micelles are equivalent as far as the distribution of surfactant species is concerned and $f_0 = f_p$.

(ii) In the limit $\sigma \ll 1$, eqs 4, 6 lead to a quadratic equation for $f_p$

$$ x_p(1 - e^{-\epsilon})f_p^2 + [1 - (f + x_p)(1 - e^{-\epsilon})]f_p = fe^{-\epsilon} $$

from which a simple analytical solution for $f_p$ is readily obtained. The solution that corresponds to this limit are plotted as two dotted curves (for $f_p$ and $f_0$) on Figure 2. The agreement with the numerical solution is better for the smaller value of $\sigma$ (Figure 2b).


Figure 3. Values of $f$ at the points where $f'_0 = 0.1$ (bottom solid curve), $f'_0 = 0.5$ (middle solid curve), and $f'_0 = 0.9$ (top solid curve) as functions of $\epsilon$ for $x_0 = 0.5$ and $\sigma = 2$ (a) or $\sigma = 10$ (b). The solid curves correspond to the full numerical solution, the dashed curves to the limit $\epsilon, \sigma \gg 1$ (eq 10) and the dotted curves to the limit $\sigma \ll 1$ (eq 12).

(iii) If both $\epsilon \gg 1$ and $\sigma \gg 1$, the entropy terms are negligible and $f'_0$ can be readily expressed as a function of $f$. Two cases need to be distinguished. For $\epsilon/\sigma < 1$ the adsorption isotherm consists of three stages:

(I) $f_p = 0$, $f_0 = \frac{f}{1 - x_p}, \quad 0 \leq f \leq (1 - x_p)\frac{\epsilon}{\sigma}$

(II) $f_p = f - (1 - x_p)\frac{\epsilon}{\sigma}$, $f_0 = f + x_p\frac{\epsilon}{\sigma}$, \quad \ \quad \quad \quad \quad (1 - x_p)\frac{\epsilon}{\sigma} \leq f \leq 1 - x_p\frac{\epsilon}{\sigma}$

(III) $f_p = \frac{f - (1 - x_p)}{x_p}$, $f_0 = 1$, $1 - x_p\frac{\epsilon}{\sigma} \leq f \leq 1$ (8)

This limiting solution is shown in Figure 2a (dashed curves). The three adsorption stages are clearly distinct: (I) amphiphiles adsorb only to the empty micelles, (II) amphiphiles adsorb to both empty and filled micelles until the empty micelles are saturated, and (III) amphiphiles keep adsorbing only to the filled micelles.

For the values used in the figure, the approximation provides only a rough approximation but as the magnitudes of $\epsilon, \sigma$ increase the approximation improves considerably. Note that the limiting solution depends only on the ratio $\epsilon/\sigma$.

If, on the other hand, $\epsilon/\sigma > 1$ the adsorption isotherm consists only of two stages:

(I) $f_p = 0$, $f_0 = \frac{f}{1 - x_p}, \quad 0 \leq f \leq (1 - x_p)$

(II) $f_p = \frac{f - (1 - x_p)}{x_p}$, $f_0 = 1$, $1 - x_p \leq f \leq 1$ (9)

This limit corresponds to strong surfactant–macronion repulsion. The two adsorption stages are as follows: (I) At first, amphiphiles adsorb only to the empty micelles until they are fully saturated. (II) In the second stage amphiphiles adsorb only to the filled micelles since no available sites remain on the empty micelles. The dashed curves in Figure 2b correspond to this limiting case. Here again the approximation improves as $\epsilon, \sigma$ increase in magnitude.

Equation 9 is also the limiting isotherm in the case of strong attractive interactions $\sigma < 0$.

The motivation of this study is the need to control the interactions between the macronion and the micellar surface as well as the interactions between the filled micelles. Both depend on the composition of the interfacial layer and it is then of interest to calculate the overall fraction $f$ of amphiphiles that is needed in order to reach a certain amphiphile composition, $f'_p$, in the filled micelles.

Typical behavior is depicted in Figure 3 where the values of $f$ at the initial stages of adsorption ($f'_0 = 0.1$; bottom solid curve), at the midpoint ($f'_p = 0.5$; middle solid curve), and at the final stages of adsorption ($f'_p = 0.9$; top solid curve) are plotted as functions of $\epsilon$ for $x_0 = 0.5$, $\sigma = 2$ in part a and $x_0 = 0.5$, $\sigma = 10$ in part b.

Once again, the limit $\epsilon, \sigma \gg 1$ proves to be a useful guide for understanding and approximating the adsorption behavior. Within this approximation

$$f(f'_p) = \begin{cases} f'_p + (1 - x_p)\frac{\epsilon}{\sigma} & \frac{\epsilon}{\sigma} \leq f'_p \\ 1 - (1 - f'_p)x_p & f'_p \leq \frac{\epsilon}{\sigma} \end{cases}$$ (10)

while the onset of adsorption onto the filled micelles occurs when

$$f(f'_p = 0) = \begin{cases} (1 - x_p)\frac{\epsilon}{\sigma} & \frac{\epsilon}{\sigma} \leq 1 \\ (1 - x_p) & 1 \leq \frac{\epsilon}{\sigma} \end{cases}$$ (11)

Similarly, in the limit $\sigma \ll 1$, one can obtain a similar relation from eq 7 yielding

$$f(f'_p) = \frac{1 - x_p(1 - f'_p)(1 - e^{-\epsilon})}{f'_p + (1 - f'_p)e^{-\epsilon}} f'_p$$ (12)

The two approximations are depicted in Figure 3; the dashed curves correspond to eq 10 while the dotted curves correspond to eq 12 and can barely be distinguished from the numerical solution except for the case where $\sigma = 10$ and $f'_p = 0.1$ (Figure 3b). Note that deviations of the approximations from the exact solution are most pronounced at small values of $f'_p$. This is because at the initial stages of adsorption the isotherm is determined by a delicate balance between entropy, the amphiphile–macronion interactions, and the amphiphile–amphiphile interactions. At large values of $f'_p$, the empty micelles are near saturation, and the adsorption isotherm depends only weakly on the interaction parameters.

The main implication for designing experiments with mixed amphiphilic systems is that amphiphilic additives are not expected to be uniformly distributed throughout
the system. That is, the filled and empty micelles have different surface compositions as predicted here. Consequently, one needs to use more added amphiphiles than expected in order to reach a predefined level of surface composition in the filled micelles.

III. The Interaction Parameters

We now proceed to a microscopic derivation of the phenomenological interaction parameters $\epsilon$ and $\sigma$, that account, respectively, for the amphiphile–macroion and amphiphile–amphiphile interactions in these mixed-amphiphile systems.

In our definition of the free energy (eqs 1 and 2), the term linear in $f_p$ and its coefficient $\epsilon$ represent the interaction of the amphiphiles with a macroion, while the terms quadratic in $f_p, f_0$, and their coefficient $\sigma$ account for the lateral interactions among the amphiphiles. However, this distinction is not necessarily always valid. For example, in the presence of long-range interactions, the linear and quadratic terms in the free energy may mix contributions from both surfactant–macroion and surfactant–surfactant interactions. In the case of Coulomb interactions, the range of the interaction depends on the presence of salt inside the micelles. The mobile salt ions adjust their local concentrations and thus screen the Coulomb interactions. For simple, monovalent, salt the electrostatic screening length $\kappa^{-1}$, is related to the salt concentration $c_b$ via

$$\kappa^2 = \frac{8\pi l_B c_b}{(13)}$$

where $l_B = e^2/\kappa_0 k_BT$ is defined as the Bjerrum length, $e$ being the elementary charge and $\epsilon_0$, the dielectric constant of water. In the limit where the electrostatic screening length, $\kappa^{-1}$, is smaller than the other length scales in the system (such as $R_0, R$), the electrostatic interactions are effectively short ranged and $\epsilon$ and $\sigma$ can be calculated analytically. As shown below, in this limit, the surfactant–macroion interactions and the surfactant–surfactant interactions are separable from each other.

When screening is weak (and $\kappa^{-1}$ large) electrostatic interactions are long-ranged and the calculation is more involved. In principle, one could either calculate the free energy numerically (see, e.g., ref 14) or, alternatively, use various approximations, such as the two-phase approximation, to estimate the coefficients $\epsilon$, $\sigma$ (see, e.g., refs 15–19).

A. The Debye–Hückel Limit.

A simple representation of the experimental system is a spherical macroion of radius $R_0$, carrying $Z_0$ charges on its surface and located at the center of a spherical micelle of radius $R$. The spherical macroion can represent a globular protein or a spherical globule. Here the interacting amphiphiles that are added to the amphiphilic layers are charged surfactants. The interfacial layer then consists of a fraction $f_p$ of charged surfactants and a fraction $1 - f_p$ of neutral ones. The area per surfactant is $\pi a^2$. We assume, for simplicity, that the small ions inside the micelle are in contact with a salt reservoir at a fixed concentration, $c_b$. The Poisson–Boltzmann equation that describes the electrostatic potential $\psi$ inside the micelle is then

$$\nabla^2 \psi = \frac{8\pi \epsilon_0 c_b}{\epsilon_0} \sinh \frac{\psi}{k_B T}$$

(14)

In the limit of strong screening the electrostatic potential is small compared with the thermal energy, $\gamma = \psi/k_B T \ll 1$, and eq 14 can be linearized, yielding

$$\nabla^2 \gamma = \kappa^2 \gamma$$

(15)

The solution to eq 15 in spherical symmetry is of the form

$$y(r) = \frac{A}{r} e^{\gamma r} + \frac{B}{r} e^{-\gamma r}$$

(16)

where $r$ is the distance from the center of the spherical micelle. The coefficients $A$ and $B$ can be determined from the boundary conditions. At the macroion surface:

$$\frac{dy}{dr} \bigg|_{r=R_0} = -\frac{4\pi l_B Z_0}{4\pi R_0^2}$$

(17)

while at the micellar surface

$$\frac{dy}{dr} \bigg|_{r=R} = -\frac{4\pi l_p f_p}{\pi a^2}$$

(18)

For simplicity we have assumed that the charges are uniformly distributed on the surfaces of the macroion and the micelles. Although our system maintains global neutrality, individual micelles can carry some excess charge as was demonstrated by conductivity experiments. Indeed, because of the low dielectric constant of oil the energy associated with a net micellar charge is as much as 40 times higher than in water. It is therefore reasonable for our purpose here to assume that the micelle and its contents are overall neutral so that the electric field vanishes inside the micelle. Since the electric field does not penetrate the oil phase the dielectric properties of oil do not enter the calculation.

The excess free energy of a micelle carrying $N = 4\pi R^2/\pi a^2$ surfactant molecules is now given by (see, e.g., ref 20):

$$N\Delta\Omega = \int d\mathbf{r} \left\{ \frac{1}{8\pi l_B} (\nabla y)^2 + \sum_{i=\pm} c_i [\log(c_i/c_b) - 1] + 2c_b \right\}$$

(19)

where $c_\pm = c_b \exp(\mp \gamma y)$ and $y(r)$ is the solution to eqs 16–18.

In the Debye–Hückel limit, $y(r) \propto 1/r$, and in spherical symmetry the free energy per surfactant becomes

$$\Delta\Omega/N = 1/\int_{R_0}^{R} dr 4\pi r^2 \left\{ \frac{1}{8\pi l_B} \frac{dy^2}{dr} + c_b y^2 \right\}$$

(20)

$$= \omega_0 + f_p \left[ \frac{\sigma}{2} + \frac{1}{2} \right]$$

(21)

where $\omega_0$ is a composition-independent term. The above expression for $\Delta\Omega/N$ is essentially equivalent to eqs 2 and 2 up to this composition-independent term. From the solution one extracts

\[
\epsilon = \frac{2k_l l_b Z_0 e^{-\kappa(R-R_0)}}{(kR - 1)(kR + 1) - (kR + 1)(kR_0 - 1)e^{-2\kappa(R-R_0)}}
\]

(22)

\[
\sigma = \frac{4\pi l_b^2 R}{\pi a^2} \times \frac{\kappa R_0 + 1 + (\kappa R_0 - 1)e^{-2\kappa(R-R_0)}}{(kR - 1)(kR + 1) - (kR + 1)(kR_0 - 1)e^{-2\kappa(R-R_0)}}
\]

(23)

Indeed, the fact that the only dependence on the charge \(Z_0\) is linear and appears only in the term that is linear in \(f_0\) reflects the short-range nature of the electrostatic interactions in the Debye–Hückel regime.

The results, eqs 22 and 23, are reminiscent of the free energy of interaction between two flat surfaces in the Debye–Hückel limit, as can be verified in the limit \(R - R_0 \ll R_0\).

In this limit \(R \gg R_0 \gg \kappa^{-1}\), eq 22 reduces to

\[
\epsilon \approx \frac{2l_b^2 Z_0 e^{-\kappa(R-R_0)}}{R(kR_0 + 1)}
\]

(24)

Note that this energy is twice the electrostatic interaction energy of a single charged surfactant with the macroion. The reason is that \(\epsilon\) accounts for the total amphiphile–macroion interactions and thus also includes the contributions of the counterions that are added to maintain charge neutrality whenever a charged surfactant replaces a neutral one. The counterion contribution is a balance of entropy and electrostatic energy that turns out to be equal to the electrostatic energy of a charged surfactant.

In the same limit, eq 23 reduces to

\[
\sigma \approx \frac{4\pi l_b^2 \kappa^{-1}}{\pi a^2}
\]

(25)

which is independent of \(R\) and \(R_0\) when the screening length is short.

In this limit the ratio \(\epsilon/\sigma\) is given by

\[
\frac{\epsilon}{\sigma} \approx \frac{2Z_0 e^{-\kappa(R-R_0)}}{N(kR_0 + 1)}
\]

(26)

As can be expected, unless \(Z_0\) is extremely large, the interaction of the charged surfactant with the macroion is negligible in the limit where \(R - R_0 \gg \kappa^{-1}\), and no partitioning occurs between the empty and filled micelles. In this limit, the system is located close to the left-hand edge of Figure 3. The same behavior is observed in the limit where \(Z_0 \ll N\), provided that \(R\) and \(R_0\) are of the same order of magnitude.

In the opposite limit, \(\kappa^{-1} \gg R \gg R_0\), eqs 22 and 23 reduce to

\[
\epsilon \approx \frac{Z_0}{2c_b V}
\]

(27)

\[
\sigma \approx \frac{N}{2c_b V}
\]

(28)

where \(V = (4\pi/3)(R^3 - R_0^3)\) is the free volume inside the micelle.

Both \(\epsilon\) and \(\sigma\) (eqs 27 and 28) diverge at low salt concentrations \((c_0 \rightarrow 0)\). This can be explained by the following simple argument. First, we recall that this limit corresponds to the limit of long-range electrostatic interactions and therefore is not rigorously consistent with the Debye–Hückel limit. However, if \(Z_0\) is small enough, the rescaled electrostatic potential, \(\gamma(R)\), is low enough to indeed justify linearizing the Poisson–Boltzmann equation, eq 14, and the limit of \(k \rightarrow 0\) is meaningful. In this case, the electrostatic interactions inside the micelle are negligible and the main contribution to the free energy arises from the confinement of the counterions to the micelle. Taking into account that, in the limit of weak electrostatic interactions, the difference in ion concentration between the micelle and the bulk is very small, \(\delta c/\delta c_b \ll c_b\), one can expand the entropic contribution to the free energy, eq 19, in powers of \(\delta c/\delta c_b\). The leading contribution is of second order:

\[
\frac{\delta \Omega}{N} \approx \frac{V}{N \sum_{N_f=2}^{\infty} \frac{\delta c_{\pm}^2}{2b}}
\]

(29)

From the divergence of the free energy as \(1/c_b\), eq 29, the behavior of the amphiphile–macroion and the amphiphile–amphiphile interaction energies, \(\epsilon\) and \(\sigma\), at low salt concentrations (eqs 27 and 28) becomes apparent. Furthermore, inserting \(\delta c = -\delta c_b = -(Z_0 + Z_b)/2V\) and \(Z_b = N f_b\), in eq 29 leads immediately to eqs 27 and 28.

In this regime, the ratio between the two interaction energies is

\[
\frac{\epsilon}{\sigma} \approx \frac{Z_0}{N}
\]

(30)

The ratio depends only on the number of charges on the macroion and the number of sites on the micellar surface. In the limit \(Z_0 \ll N\), the interaction of the charged surfactants with the macroion is negligible and no partitioning occurs between the empty and filled micelles. The system is located close to the left-hand edge of Figure 3. In the opposite limit, \(Z_0 \gg N\), the interaction of the charged surfactants with the macroion dominates over the interactions between the charged surfactants, and the system is located in the right-hand side of Figure 3.

**B. Rodlike Macroion.** We now proceed to estimate \(\epsilon\) for a rodlike macroion. This may apply to DNA molecules that are shorter than their persistence length (50 nm). Because of the more complicated geometry we present a simpler argument that provides only the electrostatic contribution to \(\epsilon\). Regarding \(\sigma\), one can use eq 25 as an estimate in the limit where \(\kappa^{-1}\) is small enough.

For a rodlike macroion of length \(l\), carrying \(Z_0\) charges and centered inside the micelle the interaction of charged surfactant (averaged over the micellar surface) with a differential rod element of length \(dx\) and located a distance \(x\) from the center of the rod is

\[
\delta \epsilon(x) = \frac{Z_0 l_b}{2x R} [e^{-x(R-x)} - e^{-x(R+x)}] \frac{dx}{I}
\]

(31)

Integrating over all rod elements gives the interaction energy

\[
\epsilon = 2\xi \text{ Shi}[\kappa l/2] e^{-\kappa R}
\]

(32)

where \(\text{Shi}(z) = \int_0^z dz \sinh(x)/x\) is the hyperbolic sine integral and \(\xi = Z_0 l_b/2l\) is the Manning parameter, a
dimensionless quantity that characterizes the electrostatic attraction energy of a monovalent counterion to a charged rod (see, e.g., ref 19).

In the limit $kl \ll 1$, eq 32 reduces to eq 24 with a pointlike charge ($R_0 \to 0$). In the opposite limit of strong screening one obtains

$$
\epsilon \approx 2\xi^2 \frac{e^{-\xi(R - l/2)}}{\kappa R}
$$

Using eq 25 one obtains the following estimate

$$
\frac{\epsilon}{\alpha} \approx \frac{2\xi^2 R e^{-\xi(R - l/2)}}{N_y kl}
$$

This limit is analogous to that obtained in eq 26. In the limit where $R - l/2 \gg \kappa^{-1}$, unless $\xi$ is very large, the interaction of the charged surfactant with the charged rod is negligible and no partitioning occurs between the empty and filled micelles. The system is located close to the left-hand edge of Figure 3. Similar behavior is obtained if $\xi \approx N_k d_0/R$, and since $l$ cannot exceed $R$, it is enough to require that $\xi \approx N_k d_0$.

This calculation can be generalized to the case where the rod is not centered in the micelle. In this case the interaction is given by

$$
\epsilon(y) = \xi \left( \text{Shi}[\kappa(R - y)] + \text{Shi}[\kappa(l + y - R)] \right) e^{-\xi R}
$$

where $y$ is the distance of the rod end from the micelle surface ($0 \leq y \leq R - l/2$). Equation 35 is useful in estimating the electrostatic barrier that prevents a charged rod from approaching the micelle surface

$$
\Delta \epsilon = \epsilon(0) - \epsilon(R - l/2)
$$

In the limit of weak screening, where $kl$ is small, the barrier is independent of $l$

$$
\Delta \epsilon \approx \frac{1}{6} \int_0^{l}(\xi kl)^2 R \kappa^{-1} e^{-\xi R}
$$

whereas in the limit of strong screening it is

$$
\Delta \epsilon \approx \frac{\xi}{(\kappa R)^2}
$$

For DNA, for example, $\xi = 4.2$, and the length of a short segment can be somewhere between 30 and 70 nm. The persistence length of DNA (50 nm) implies that on these length scales the molecule is basically rigid and the micelle size has to be at least as big as the DNA length. In order for the barrier $\Delta \epsilon$ (eq 38) to be considerable the screening length has to be on the order of the micelle size. For comparison, under regular physiological conditions the screening length is $\kappa^{-1} \approx 1$ nm.

C. Amphiphilic Diblock Copolymers. Amphiphilic diblock copolymers consist of long hydrophobic polymer chains that are chemically attached to hydrophilic chains. Like smaller surfactants molecules, amphiphilic diblock copolymers preferentially adsorb to the water/oil interface (Figure 1). Furthermore, recent studies have shown that amphiphilic block copolymers strongly enhance the stability of microemulsions.26 In addition, because of steric interactions, the hydrophobic block can keep the micellar contents away from the water/oil interface, while the hydrophobic block can stabilize the micelles against collisions. It is therefore useful to implement our adsorption model to the case where the added amphiphiles are diblock copolymers. For this purpose, we present in this section simple estimates of $\epsilon$ and $\sigma$ for amphiphilic diblock copolymers.

To simplify the discussion, we consider the limiting case of low curvature, where the water/oil interface can be considered as flat. This limit is valid when the copolymer dimensions (see below) are small compared with the micellar radius, $R$. We adopt a scaling approach where numerical coefficients are omitted and the emphasis is on the functional dependence of the quantities of interest (e.g., the free energy) on the physical properties (chain length, copolymer density, etc.).

We begin with the dilute regime of low copolymer density, where the fraction of sites, $f_p$, at the micellar surface that are occupied by copolymers, is low. Since the copolymer is amphiphilic, it adsorbs with the hydrophobic part immersed in the oil phase and the hydrophilic part immersed in the aqueous interior. Each block is thus in a good solvent in which the chain tends to swell and maximize monomer—solvent contacts. In the dilute regime, each polymer chain is well-separated from its neighbors, its shape resembles a mushroom, and can be described as a half sphere of radius $R_p$ (Figure 4).

The free energy of a grafted polymer chain consisting of $N_p$ monomers of size $a_p$ can be written as

$$
F = R_p^2 \frac{N_p^2}{N_p a_p^2} \frac{N_p^2}{2} R_p^3
$$

The first term is the elastic contribution of stretching the chain beyond its ideal chain size, while the second term reflects the effective monomer–monomer repulsion. Here and below we adopt an approximation introduced by


Flory,\textsuperscript{23} which has the advantage of highlighting how the different contributions to the free energy come into play. Despite its crude and approximate nature, the Flory method is surprisingly good since it overestimates both contributions to the free energy, eq 39.

Minimizing the free energy, eq 39, with respect to \( R_p \) yields the equilibrium polymer size

\[
R_p = N_p^{3/5} a_p \quad (40)
\]

The above calculation applies to both the hydrophilic and hydrophobic blocks. Since the amphiphilic copolymer need not be symmetric, one block can be longer than the other and occupy a larger volume. The larger block will dominate the polymer—polymer interaction term. In the mushroom regime, the chains are isolated from each other, but since they are free to move on the micellar surface, they form a dilute, two-dimensional, gas. Because of excluded volume interactions, different chains cannot pass through each other and the second virial coefficient, which characterizes the interchain repulsions, scales as the area occupied by a single chain, \( \pi R_p^2 \). Within a low-density virial expansion, the lowest contribution of these repulsive interactions to the free energy (per surfactant site) is

\[
F_{\text{int}} \approx \frac{R_p^2}{2a^2} f_p^2 \quad (41)
\]

This yields the following estimate for the interaction parameter \( \sigma \):

\[
\sigma \approx \frac{R_p^2}{a^2} \quad (42)
\]

It is clear from the above equation that if \( a_p \approx a \), then \( \sigma \sim N_p^{0.5} \) can be quite large. On the other hand, since in the mushroom regime the area per chain, \( \pi a^2 f_p \), is greater than \( \pi R_p^2 \), the regime is limited to

\[
f_p \approx \frac{a^2}{R_p^2} \quad (43)
\]

and the overall contribution of the interaction term to the free energy is small, on the order of \( a^2 R_p^2 \).

As demonstrated in Figure 1, the hydrophilic blocks that are adsorbed onto the filled micelles interact with its content. If the contents are modeled as a hard sphere of radius \( R_0 \), that excludes the amphiphiles, the polymer chains will be squeezed to a size smaller than their equilibrium size \( R_p \). The repulsive energy associated with the confinement of the chains to a thin layer of width \( h = R - R_0 < R_p \) is

\[
F_{\text{rep}} = \frac{(R_p^2)}{h^{5/3}} f_p \approx N_p \left( \frac{a_p}{h} \right)^{5/3} f_p \quad (44)
\]

This equation can be derived with the help of the so-called “blob” picture:\textsuperscript{24} when a polymer chain is confined to a slit of width \( h \), the chain configuration in space can be roughly divided into spherical blobs of size \( h \). The relation between the blob size and the number of monomers in it, \( g \), is determined by the solvent quality; \( g \approx g^{5/3} a_p \), in a good solvent (vis. eq 40). The energy of each blob is comparable to the thermal energy, \( k_B T \), and the total confinement energy is simply proportional to the number of blobs, \( N_p g \), leading directly to eq 44. Note that as a result of confinement, the polymer is further extended in the direction parallel to the surface.\textsuperscript{27} The blob picture is valid as long as \( g \gg 1 \), which is equivalent to \( h \gg a_p \).

From eq 44 we obtain an estimate of the interaction parameter \( \epsilon \):

\[
\epsilon \approx \left( \frac{R_p^2}{h} \right)^{5/3} \quad (45)
\]

which is larger than (but on the order of) unity since \( h < R_p \) and increases monotonically as \( h \) decreases.

We can now readily obtain an estimate for the ratio

\[
\frac{\epsilon}{\sigma} \approx \frac{\pi a^2}{h^{5/3} R_p^{1/3}} \quad (46)
\]

The ratio is small since \( a \) is a molecular length scale while \( h \) and \( R_p \) are mesoscopic length scales. As emphasized above, in the mushroom regime the energies involved are low compared with the thermal energy. This is no longer the case in the high-density regime.

Above the mushroom overlap density, i.e., for \( f_p \approx a^2 R_p^2 / 2 \), the polymers coat the surface with a uniform layer of thickness \( h \). The layer thickness is determined, as in the mushroom regime, by a balance between the elastic energy of the chains and the short-range monomer–monomer repulsion. The free energy of a brush (per chain) reads\textsuperscript{25,26}

\[
F_{\text{brush}} = \frac{h^2}{N_p a^2} + \frac{a_p^3}{2} \frac{N_p^2}{h \pi a^2 f_p} \quad (47)
\]

where \( h \pi a^2 f_p \), the average volume per chain, replaces \( R_p^3 \) in eq 39. Minimizing the free energy with respect to \( h \) yields the equilibrium brush size

\[
h^* \approx \frac{a_p^{5/3}}{(\pi a^2)^{2/3} f_p^{1/3} N_p} \quad (48)
\]

The linear dependence on \( N_p \) indicates that the chains in the brush are stretched. The free energy of a brush (per surfactant site) is now

\[
F^+ = \frac{a_p^{4/3}}{(\pi a^2)^{2/3} f_p^{5/3} N_p} \quad (49)
\]

Because of the long-range nature of chain connectivity, the free energy, eq 49, is not an integer power of \( f_p \). Although our adsorption model, eqs 1 and 2, includes only linear and quadratic powers of \( f_p \) and \( f_0 \), it can be easily generalized by adding noninteger terms. For example, a term proportional to \( f_p^{0.5} \) can be added to the free energy of the empty micelles, \( F_0 \), to account for polymer brushes extending inward and outward from the micellar surface. Similarly, a term proportional to \( f_p^{5/3} \) can be added to the free energy of the filled micelles, \( F_p \), to account for a brush extending outward from the micellar surface.

The term accounting for a brush extending inward in the filled micelles depends on whether the brush interacts with the micellar contents (macroion, polymer, etc.) or not. If the brush is unperturbed by the contents it will add to the free energy a term proportional to \( f_p^{5/3} \), independent of the micellar contents. On the other hand, if it is compressed by the micellar contents to a size \( h \lesssim h^* \) (see

\footnote{In a narrow slit, the blobs can be viewed as a rescaled polymer that forms a two-dimensional self-avoiding walk, and the new size is \( R/(h) = (Ng)^{0.4} h = a_p^{0.4} N^{0.2} h^{0.4} \).}
If the compression is weak so that $h \ll h^*$, then $\epsilon$ and $\sigma$ both scale as $N_p^{1/2} a_p$. Such large values for both parameters justify our neglect of the entropy term and the approximation eqs 8 and 9 can be used. Note that here both $\epsilon$, $\sigma$ are affected by the presence of the macroion. This, again, reflects the long-range nature of the interactions in the brush. Because of this mixed dependence, the coefficient of the quadratic term in the free energy, $\sigma$, is not the same in filled micelles (eq 1) and the empty ones (eq 2). The adsorption model can be easily adapted to allow for such differences.

Upon compression the interaction parameter, $\epsilon$, first decreases, then reaches unity when the chain resums its ideal size, $N_p^{1/2} a_p$, but if the layer is further compressed, $\epsilon$ increases again as the brush is compressed below the ideal chain size. This compression is similar to the one described by eq 44 and can be accounted for by adding a term of the form $N_p a_p^2 / h^2$ to the free energy, eq 47. It then follows that under strong compression, $h \ll N_p^{1/2} a_p$

$$\epsilon \approx \frac{N_p a_p^2}{h^2}$$  \hspace{1cm} (52)

In contrast, the two body term, $\sigma$, increases monotonically under compression. The ratio between the two parameters depends on the degree of compression

$$\frac{\epsilon}{\sigma} \approx \left( \frac{\pi a_p^2}{N_p a_p} \right)^3 h \gtrsim N_p^{1/2} a_p$$  \hspace{1cm} (53)

For weak and moderate compressions the ratio is of order unity and as the brush is further compressed the ratio substantially decreases, until it reaches a minimum on the order of $1/N_p^{3/2}$ around $h \sim N_p^{1/2} a_p$. For strong compressions, the ratio increases again, but its magnitude remains low even when the compression is unphysically large.

To simplify the discussion we considered here only the low curvature limit. Corrections to the free energy due to curvature are on the order of $h/R$. The effect of curvature should be taken into account if the brush size $h$ or the polymer extension $R_p$ are comparable to the micellar radius, $R$. Curvature is also important when the presence of the amphiphilic polymers plays a substantial role in the energetics of the water/oil interface, and is expected to affect the micellar size.

In the opposite limit where the chains that extend into the oil phase are much longer than micellar dimensions, $R_p \gg R$, the decorated micelle resembles a star polymer, in which all the branches are attached to a single central point. Interactions between different branches are long ranged and the free energy includes noninteger powers of the amphiphile concentration.

Finally, we note that eq 47 is a mean-field-like approximation that does not take into account correlations between polymer segments. More refined theories give expressions similar to eq 47, where the linear term is replaced by $f_p^{54}$ and the quadratic term is replaced by $f_p^{94}$ (see, e.g., ref 35).

IV. Conclusions and Extensions

Motivated by recent experimental approaches to confine biochemical reactions in water-in-oil, swollen micelles (microemulsions), we have predicted in this work, the composition and stability of micelles that contain a mixture of two amphiphilic species. One species (here termed the interacting amphiphile), interacts with the chemical contents (e.g., DNA in the water interior) in order to keep the contents away from the droplet surface. We have introduced a simple adsorption model to study the partitioning of two species of amphiphilic molecules between two types of micelles with different surface amphiphile compositions, depending on whether the micelles are filled or empty. We find several adsorption scenarios depending on the strength of the contents–amphiphile and amphiphile–amphiphile interactions. For example, we find that when one of the species is strongly repelled by the contents of the filled micelles, it will first adsorb on the surface of the empty micelles. The interacting amphiphile will only adsorb on the surface of the filled micelles once the empty ones are fully saturated with interacting amphiphiles. When the repulsion is not too strong, adsorption consists of three stages: an initial stage where the interacting amphiphiles adsorb only on the surface of the empty micelles, an intermediate stage where they adsorb on the surface of both empty and filled micelles, and a final stage where the empty micelles are fully saturated and the interacting amphiphiles can only adsorb on the surface of the filled droplets.

We have analyzed in detail several physical examples of interacting amphiphiles and have provided some simple estimates for the interaction energies. We focused on two cases that are of particular interest for the experimental systems that motivated this study and have characterized the main physical quantities that control the strength of the amphiphile–contents interactions in these cases. In the first case, the interacting amphiphiles are charged surfactants that interact with the micellar contents and with each other via a screened Coulomb interaction of the Debye–Hückel type. In the second case the interacting amphiphiles are diblock copolymers in which the hydrophobic chain, soluble in the continuous oil phase surrounding the micelle, is attached to a hydrophilic chain favoring the water phase inside the micelle. For charged surfactants, we find that electrostatic screening by salt can strongly reduce these interactions and limit the extent of amphiphile partitioning between the two types of micelles. In the case of amphiphilic polymers we find that the hydrophilic chain has to be strongly stretched in order to exhibit considerable partitioning.

The composition of the interfacial layer has an important effect on the physical behavior within the micelles and on intermicellar interactions. Interacting amphiphiles provide means of controlling the degree of confinement of the

biochemical contents either at the center of the micelle or, alternatively, at the micellar surface. For example, charged surfactants are useful for localizing similarly charged molecules at the center of the micelle, and attracting oppositely charged molecules to the micellar surface, while amphiphilic molecules can keep macromolecules (DNA and macromonions alike) away from the micellar surface by means of steric repulsions. To take advantage of this confinement effect, it is therefore important to understand how the amphiphiles are partitioned between the empty and filled micelles.

In many cases, confinement to the center of the micelle is only one aspect of isolating the micellar contents from its surroundings. Exchange of material between different micelles needs to be controlled as well. Since kinetic exchange rates depend strongly on intermicellar interactions, it is useful to understand how these interactions depend on the composition of the interfacial layer. The treatment of intermicellar interactions between micelles containing charged surfactants or amphiphilic polymers is scattered among different articles in various fields, and for the convenience of the interested reader we present a short review of these interactions in the Appendix. Because of the low dielectric constant of oil and the subsequent absence of mobile charges in the oil phase, fluctuation-induced interactions of the van der Waals type decay very weakly and can lead to long-range intermicellar attractions. In contrast, micelles that are covered with hydrophobic chains that extend into the oil phase, repel each other due to steric repulsions between the chains. This suggests that amphiphilic chains provide an effective way to stabilize the micelles against exchange of contents.

Our simple approach can serve as a starting point for both theoretical and experimental investigations. From a theoretical point of view, we have assumed here that the size of the micelles is not affected by the contents of the micelle or the composition of the amphiphilic layer. This is not necessarily always the case. It is well-known that amphiphilic polymers can modify elastic properties, such as the spontaneous curvature, of an interfacial layer (see, e.g., ref 31). These changes may lead to changes in the micellar radii that depend on the composition of the interfacial layer. By carefully choosing the sizes of the hydrophobic and hydrophilic blocks one can either suppress or enhance this effect.

From an experimental point of view, our study provides several predictions that could be tested experimentally. For example, we can make explicit predictions for the interfacial surfactant compositions of empty and filled micelles. We demonstrated that since the surfactant composition depends on the surfactant–internal macronion interaction, the composition depends on whether there is a macronion in the micelle or not. In the case of amphiphilic polymers, for example, the effective size of the micelle depends on the density of polymer chains extending from the surface. Various experimental techniques13 including small-angle X-ray scattering,24 fluorescence quenching26 and photon correlation spectrometry22 can measure the effective micellar size and correlate it to the fraction of filled micelles. Fluorescence quenching26 can be also used to measure intermicellar exchange rates of probe and quencher molecules.

In section 3, we provide explicit predictions for the dependence of the interaction parameters $\epsilon$ and $\alpha$ and their ratio $\epsilon/\alpha$ on various physical properties, such as the amount of salt, the macronion charge and the polymer chain length. These properties can be varied systematically in order to test the predictions of the model.

Our adsorption model is very general and can be applied to many situations where two species compete with each other on two different types of binding sites. Such a situation occurs, for example, when two (or more) proteins can adsorb onto different filament types in the cell (e.g., F-actin and microtubules). Another example from biology involves gene regulatory proteins that bind to DNA molecules in order to control transcription.25 Two different proteins that can bind preferentially to different motifs on the DNA sequence (with different binding energies), might compete with other for the same binding sites. One can also consider another example in colloid science, where two polymer species with different charge or molecular weight adsorb competitively onto two types of colloids, that differ in size or charge.

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Appendix. Intermicellar Interactions

In this appendix we present a brief overview of intermicellar interactions that are of relevance to the cases discussed above. The object of this overview is to provide a short introduction and a collection of main results from different sources that could be of interest to readers that are interested in the interplay between surface composition and intermicellar interactions. For clarity, we focus on the general behavior and leave out the complications that arise from the micellar structure and contents.

A. Electrostatic Effects. Various aspects of electrostatic interactions between micelles have been studied in recent years.8,14,41–44 Here we review only the main results that are applicable to our system.

Net Micellar Charge. Because of the low dielectric constant of oil, $\epsilon_{\text{oil}} = 2$, charged micelles in oil behave quite differently than charged micelles or charged colloids in an aqueous solution.25 Not only does the low dielectric constant of oil amplify the Coulomb energy of a charged micelle but also it inhibits the presence of small charge carriers in the oil phase. The reason is the high solvation energy of small ions, which scales as $l_B^{(\text{oil})}/2a$, where $l_B^{(\text{oil})}$

(36) Recent experiments37–39 indicate that micelles of ionic surfactants have the capacity of screening electrostatic interactions in oil. This screening is due to the presence of a small fraction of charge micelles among a vast majority of neutral ones. However, because of the low concentration of these charge micelles their ability to screen electrostatic interactions is limited to distances greater than tens to hundreds of nanometers.

\( \approx 28 \) nm and \( a \approx 0.1-0.2 \) nm is the radius of a small ion. Consequently, the concentration of small charge carriers in oil is so low that screening of electrostatic interactions is practically negligible.

In the absence of screening, the electrostatic energy of a micelle carrying an excess charge \( z e \) is \(^8\)

\[
\beta U_{\text{el}}(z) = \frac{z^2 1^{(\text{all})}}{2R} \tag{54}
\]

where \( \beta = 1/k_B T \) and \( R \) is the micellar radius. As soon as the micelle size grows beyond \( 1^{(\text{all})} \), it becomes likely that it will acquire some residual charge, as indicated by conductivity experiments. \(^8\)

The distribution of charges among different micelles depends on the process used for creating the microemulsion and on the conditions at which it is kept. If the micelles are kept under conditions of thermal equilibrium, the distribution is given by a Boltzmann weight \( p(z) \sim \exp[-\beta U_{\text{el}}(z)] \). Because of the practical absence of mobile ions, all charges are confined to the micelles and the average micelle charge \( \langle z \rangle \) vanishes. However, there are thermal fluctuations in the number of net charges per micelle, whose root-mean-square is given by \(^8\)

\[
\langle z^2 \rangle^{1/2} = \left( \frac{R}{l_B^{(\text{all})}} \right)^{1/2} \tag{55}
\]

The implications of this are that a random mixture of micelles is likely to include charged micelles. Oppositely charged micelles will attract each other with a long-range \( 1/r \) potential

\[
\beta u(r) = -\frac{1}{z^2 1^{(\text{all})} l_B^{(\text{all})}} \frac{1}{r} \tag{56}
\]

and might aggregate and exchange some of their content during collisions. To avoid these long-ranged attractions it might be desirable to exclude the charged micelles from the system and leave only the neutral ones. Because of the high energetic barrier for small ions in oil, isolated micelles will remain neutral as long as they do not collide with one another.

If charges are allowed to freely exchange between micelles, the net charge of each micelle will fluctuate. Coupled fluctuation in pairs of micelles a distance \( r \) from each other lead to long-range attraction of the form \(^42\)

\[
\beta u(r) = - \left( \frac{1}{z^2 l_B^{(\text{all})}} \right)^2 = - \left( \frac{1}{R} \right)^2 \tag{57}
\]

**Micellar Polarizability.** If exchange of charges between micelles is not possible, net charge fluctuations are suppressed but micelles can still aggregate due to interactions related to the micellar polarizability, \( \alpha \). Driven by thermal fluctuations, the mobile charges inside the micelle rearrange within the micelle and give rise to instantaneous dipole moments. In an isolated micelle, these dipole moments average out to zero. However, when two micelles are near each other the electric field due to the fluctuating dipoles in one micelle enhance fluctuations in the second micelle and vice versa in a classical analogue of van der Waals interactions (see e.g., ref 46). These coupled fluctuations lower the free energy and hence lead to intermicellar attraction that is given by \(^46,47\)

\[
\beta u(r) = - \frac{3 \alpha^2 \epsilon_{\text{oil}}}{\epsilon_{\text{all}} R^4} \tag{58}
\]

In our case, the micellar polarizability is given by \(^43\)

\[
\alpha = \Theta_1 \epsilon_w \epsilon_{\text{all}} k R \epsilon_{\text{all}} R^3 \tag{59}
\]

where \( \Theta_1 = \epsilon_w / (\epsilon_w + 2 \epsilon_{\text{all}}) \) in the limit \( k R \ll 1 \) and \( \Theta_1 = 3 \epsilon_w / \epsilon_{\text{all}} k R \) in the limit \( k R \gg 1 \). \(^45\) In both cases, \( \Theta_1 \rightarrow 1 \) if the limit \( \epsilon_{\text{al}} \ll \epsilon_w \), and the interaction reads

\[
\beta u(r) \approx - 3 \left( \frac{R^6}{R^2} \right) \tag{60}
\]

This contribution decays much faster \((-1/r^6\) than the charge fluctuation contribution to the attraction \((-1/r^2\) discussed above.

**High Order Terms.** Equations 57 and 60 are special cases of fluctuation induced attractions. In the more general case, coupled fluctuations in the electrostatic multipole moments of order \( n \), \( Q(n) \), on two different micelles lead to attractions of the form \(^44,45\)

\[
\beta u(r) = - \frac{1}{2} \left[ Q_1^{(\text{all})} \right]^2 \sum_{n_1, n_2} A(n_1, n_2) \left( Q_1^{2(n_1)}(n_1) Q_2^{2(n_2)} \right) \tag{61}
\]

where \( A(n_1, n_2) = \frac{(2n_1 + 2n_2)!}{(2n_1 + 1)!(2n_2 + 1)!} \) \(^6\)

The quantities \( \langle Q^2(n) \rangle \) represent basically the linear response of a micelle to an external field. The details of the micelle composition and structure, e.g., the dielectric constant of water, enter only through these response functions.

The terms in eq 61 can be classified according to their \( r \) dependence, which is a measure of the range, and hence the strength, of the different contributions. The first term corresponds to \( n_1 = n_2 = 0 \) and scales as \( 1/r^2 \). It is due to fluctuations of the net charge (monopole) on the two micelles and is given by eq 57. The next term corresponds to \( n_1 = 0, n_2 = 1 \) and scales as \( 1/r^4 \). It represents the coupling of charge fluctuations on one micelle with dipole fluctuations on the other micelle. This term reads \(^43\)

\[
\beta u(r) = - \left[ \langle z^2 \rangle l_B^{(\text{all})} \right]^2 = - \left[ \frac{1}{2} \frac{R^4}{R^2} \right] \tag{62}
\]

The third term scales as \( 1/r^6 \) and includes two contributions. One contribution is the \( n_1 = n_2 = 1 \) term that is due to coupled dipole fluctuations on the two micelles and is given by eq 58. The second contribution is the term \( n_1 = 0, n_2 = 2 \). It is due to the coupling of fluctuations in the net charge of one micelle with the quadrupole moment of another micelle. In the limit \( \epsilon_{\text{al}} \ll \epsilon_w \) this contribution reads

\[
\beta u(r) \approx - \left[ \frac{1}{2} \frac{R^6}{R^2} \right] \tag{64}
\]

Note that if the system is prepared and maintained so that only neutral micelles remain the \( n_1 = n_2 = 1 \) term (eq 58) is the lowest nonvanishing contribution to eq 61.

**B. Effect of Grafted Chains.** As discussed above, the absence of mobile charge carriers in a low-dielectric medium leads to attractive electrostatic interactions. Because of the need to stabilize micelles against collisions we suggest here that covering the external micellar surface

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with polymer chains can be used to counter these attractions. The reason is that polymer chains give rise to intermicellar repulsions and thus prevent micelles from exchanging material. Both the range and strength of these interactions strongly depend on the length and density of the grafted polymer chains and the behavior in the different regimes can vary considerably. Generally speaking, dense layers of shorter chains lead to steeper repulsions that begin when two brushes are in contact and rise steeply as the overlap increases.\(^{48}\) In contrast, longer chains give rise to long-range softer repulsions.\(^{34,49-51}\) The two regimes are discussed below within simple scaling arguments that highlight the main features of these interactions.

We begin with the brush regime discussed in section 3.3. As mentioned above, eq 47 can be used to estimate the free energy of a compressed brush. The same expression applies for two flat brushes that are compressed against each other. In the limit of low curvature, where the equilibrium brush size is much smaller than the micellar radius, \(h^* \ll R\), the Derjaguin approximation\(^{46}\) can be used to relate the excess free energy of interaction between two flat brushes (per unit area), \(\Delta F(h) = 2F_{\text{brush}}(h) - F_{\text{brush}}(h^*)f_p/\pi a^2\), and the free energy of interaction between two spheres \(u(r)\)

\[
\beta u(r) = \pi R \int_{2R}^{\infty} dr' \Delta F(r'/2 - R) \tag{65}
\]

The resulting free energy of interaction reads

\[
\beta u(r) = \frac{3\pi R a_p^3}{2(\pi a^2)^2} \left( h - \frac{h^3 - \frac{8}{3} \ln h}{3} \right) N_p^2 f_p^2 \tag{66}
\]

where \(h = (r - 2R)/2h^*\). The interaction vanishes when the brushes begin to overlap (\(h = 1\)) and diverges when the surfaces of the two micelles touch each other (\(h = 0\)). Since \(u(r)\) scales as \(N_p^2\), the repulsion becomes very strong as soon as the two brushes overlap considerably. Note that the exact dependence on \(h\) depends on the approximation used, but the scaling remains unchanged (see, e.g., ref 26).

We now turn to the polymer star limit where the size of the grafted chains is much larger than the micellar size. In this limit the interaction between two star polymers with \(f_p = f_p N\) arms (recall that \(N = 4R^2/a^2\)) is of the form\(^{34,49-51}\)

\[
\beta u(r) = \frac{5}{18} f_p^{3/2} \times \begin{cases} -\ln(r/D) + \frac{1}{1 + \kappa_s D} & r \leq D \\ \frac{1}{1 + \kappa_s D} e^{-(D/r)} \exp[-\kappa_s(r - D)] & r > D \end{cases} \tag{67}
\]

where \(D = f_p^{1/5}N_p^{3/5}a_p\) is the diameter of the star polymer corona. It marks a crossover between a soft logarithmic potential at short distances, \(r \ll D\), and an exponentially decaying potential at large distance, \(r \gg D\). The decay length of the large distance behavior is given by \(\kappa_s^{-1} \sim D/\sqrt{f_p}\). The interaction is now much softer and exhibits much weaker dependence on the chain length \(N_p\).

C. Additional Contributions. In addition to the contributions described in the preceding sections, inverted micelles can show short-range attractions over a range comparable to the length of a surfactant molecule.\(^{52}\) The exact mechanism for this interaction is not exactly clear. Two sources may contribute to this attraction; it can be due to the mutual interpenetration of surfactant tails, or to the perturbation the micelles induce in the otherwise uniform distribution of surfactant molecules in the oil phase.\(^{52}\) In the second scenario, the attraction between the tails of the surfactant molecules that are dispersed in the oil phase and the tails in the micellar corona (see Figure 1) induces a concentration gradient around the micelles. This concentration gradient causes a free energy increase that can be reduced by bringing the two micelles closer to each other. This mechanism is analogous to that leading to depletion mediated attractions.\(^{53}\)

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