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Notes

An Interfacial Curvature Map for Homopolymer Interfaces in the Presence of Diblock Copolymers

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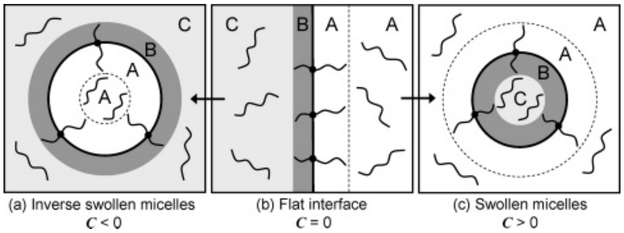
Introduction

Water and oil, two highly immiscible liquids, can be made compatibilized by adding an amphiphilic compound such as a soap or detergent to create a microemulsion of oil in water, water in oil, or a bicontinuous phase of water and oil. The term “microemulsion” was first used to describe these phases in 1959,[1] but it has been known for over 100 years that adding a third compound to two immiscible compounds can increase their mutual solubility if that particular compound is equally soluble in the other two.[2] Today, microemulsions are receiving ever-increasing attention as it becomes clear how useful they are for drug delivery, oil recovery, many types of chemical reactions, and many other applications.[3−8]

In the late 1990s, polymeric bicontinuous microemulsions were discovered in ternary systems of A homopolymer, B homopolymer, and a symmetric AB copolymer,[9−24] and they have received much attention due to their applicability to blend compatibilization and the formation of composites with improved mechanical or electrical properties. While most attention has been placed on the bicontinuous microemulsion phase, cylindrical and spherical micellar microemulsion phases are also important to consider because of their ability to encapsulate droplets of one material in another. Polymeric micellar microemulsions may be useful in many applications, from polymer−nanoparticle composites to drug delivery.

Bicontinuous microemulsions can be formed with blends of a symmetric AB diblock copolymers and equal amounts of corresponding homopolymers.[11,25] It has also been recognized that the introduction of favorable interactions between the B copolymer block and one of the homopolymers phases provides enhanced flexibility in the design of microemulsions and compatibilized polymer blends.[14,21,26−28] In our nomenclature we account for this by replacing the B homopolymers with a C homopolymer. A characteristic of bicontinuous microemulsion phases is that the spontaneous interfacial curvature characterizing the interface between the A- and C-rich regions is equal to zero, or very nearly so. Systems with a substantial spontaneous curvature will tend to form either the micellar or inverse micellar phases illustrated in Figure 1. The first possible structure is a flat interface between the A and C homopolymers with the AB copolymer adsorbed at the interface, shown in Figure 1b. This is the equilibrium state when the copolymer is symmetric and when the interactions are “balanced” to give a spontaneous interfacial curvature of zero.[29] A second possible structure is a swollen micelle, shown in Figure 1c. The swollen micelle is an AB copolymer micelle that forms in the A homopolymer matrix with C homopolymer solubilized in its core. Swollen micelles form when the spontaneous curvature of the copolymer interface is bent inward toward the shorter B block. The third possible structure is an inverse swollen micelle, shown in Figure 1a, which forms when the B−C attractive interactions are strong enough so that the micelle inverts and forms in the C matrix to maximize the B−C contacts. In an inverse swollen micelle, the B block forms the corona, and the A block and solubilized A homopolymer form the core.



(a) Inverse swollen micelles
$C < 0$
(b) Flat interface
$C = 0$
(c) Swollen micelles
$C > 0$

Figure 1. Schematics of the three possible structures that can form in a system of an asymmetric AB copolymer, A homopolymer, and C homopolymer, where B and C have favorable interactions and the fraction of B in the copolymer is small. (a) Inverse swollen micelles, (b) flat interface, (c) swollen micelles.

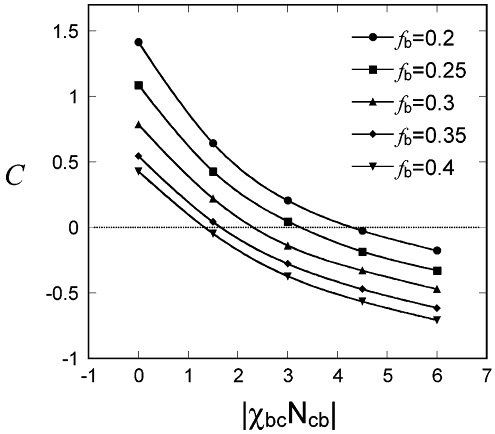


Figure 2. Equilibrium curvature C as a function of $|\chi_{bc}N_{cb}|$ for f_b = 0.2−0.4.

The three structures in Figure 1 correspond to three different values of the normalized interfacial curvature, C, which we define in the following way:

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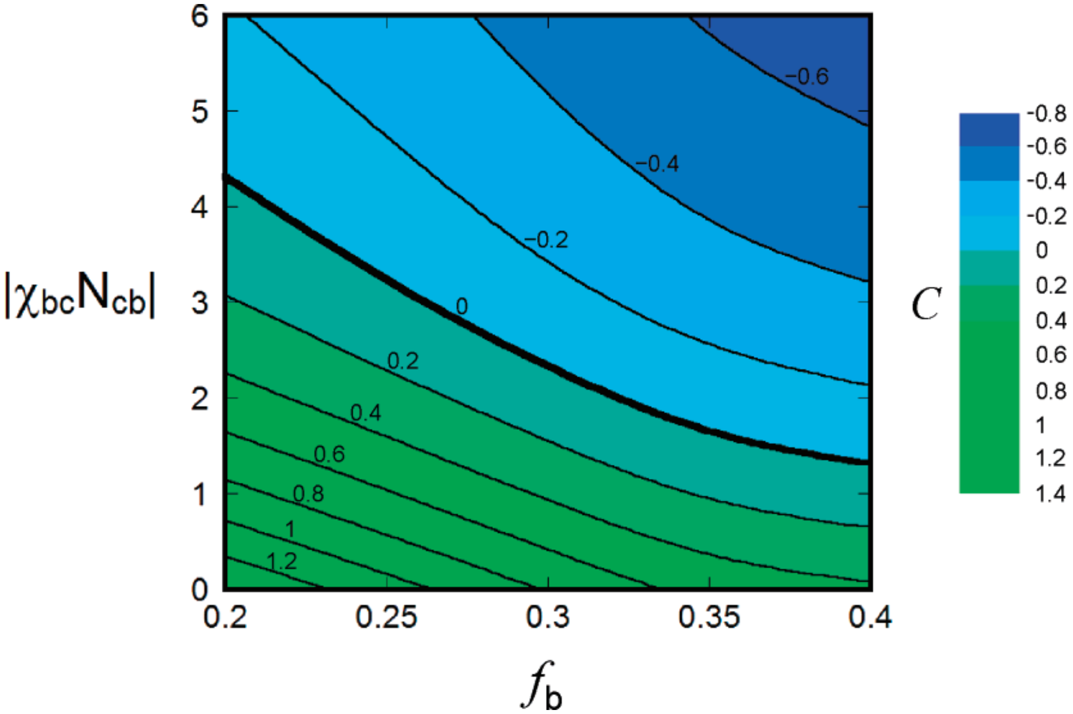

Figure 3. Phase diagram for the equilibrium curvature as a function of f_b and $|\chi_{bc}N_{cb}|$. The contour lines correspond to values of C. Blue regions represent A-centered inverse swollen micelles ($C < 0$), and green regions represent C-centered swollen micelles ($C > 0$).

$$C = \frac{R_0}{R_i} = \frac{aN^{1/2}}{R_i} \tag{1}$$

Here R_0 is the unperturbed rms end-to-end distance of the copolymer, R_i is the radius of the swollen or inverse swollen micelle, N is the copolymer degree of polymerization, and a is the statistical segment length. A curvature of 0 corresponds to a flat interface, while $C > 0$ is defined as a swollen micelle and $C < 0$ is an inverse swollen micelle. The spontaneous interfacial curvature can be obtained from self-consistent mean-field theory, as outlined by Matsen[30] and Müller and Gompper.[31] The complete structure of periodic phases can also be calculated from SCF theory, as has been done recently by Denesyuk and Gompper for AB homopolymer blends with added AC copolymer.[29] Self-consistent-field theory has also been used by Balsara et al. in order to extract information from emulsified blend systems that this group has developed.[21,27,32] These authors showed that a variety of equilibrium phases can be formed, based on the degree of homopolymers incompatibility, the constituent molecular weights, and nature of the interactions between the B and C components.

In this Note we develop an interfacial curvature map quantifying the dependence of the interfacial curvature on the copolymer symmetry and the strength of the BC interaction. Our implementation of the self-consistent-field approach is equivalent to that of Matsen[30] and has been outlined in a previous publication.[33] We assume in our calculations that the total degrees of polymerization, N, of all three polymers are equal to one another and that the A homopolymer is highly incompatible with both B and C. Specifically, we choose $\chi_{ab}N = \chi_{ac}N = 40$, where χ_{ij} is the Flory interaction parameter describing the interaction between repeat units of component i and component j. The interfacial curvature is determined by f_b, the volume fraction of B in the AB diblock copolymer, and the favorable interactions between the B and C components, which we express in terms of the quantity $\chi_{bc}N$.

Results and Discussion

Equilibrium spontaneous curvatures were calculated for values of f_b ranging from 0.2 to 0.4, and the results are shown in Figure 2 in a plot of the normalized interfacial curvature vs $|\chi_{bc}N_{cb}|$. When the fraction of B is increased to 0.35 and 0.4, the curvature is shifted toward the A-centered inverse swollen micelles because the higher amount of B in the copolymer helps to stabilize the inverted curvature. When f_b is decreased, the curvature is shifted toward the regime corresponding to swollen micelles. With a smaller fraction of B, the copolymer can most easily stabilize small B- and C-centered micelles. At $f_b = 0.2$ and $\chi_{bc}N_{cb} = 0$, the curvature of the interface is $C = 1.4$, corresponding to a highly curved interface with $R_i = 0.71R_0$. This swollen micelle is almost as small as an unswollen AB copolymer micelle with $f_b = 0.2$, which has $C = 1.7$ ($R_i = 0.58R_0$).

The data in Figure 2 can be plotted as a three-dimensional curvature map with f_b and $|\chi_{bc}N_{cb}|$ on the x and y axes, respectively, and C as the third dimension, represented by contour lines as shown in Figure 3. The phase diagram shows two main regions: one of C-centered swollen micelles (bottom left) and one of A-centered inverse swollen micelles (top right). The regions are separated by a line where the spontaneous curvature is zero. At low values of f_b and $|\chi_{bc}N_{cb}|$, swollen micelles are favored, but as one or both of the parameters are increased, the equilibrium curvature shifts toward inverse swollen micelles.

We note that the curvature increases at a much faster rate in the swollen micelle region than in the inverse swollen micelle region. At similar distances from the zero-curvature line, the positive curvature reaches $C = 1.2$ while the negative curvature only reaches $C = -0.6$. Because the fraction of B in the copolymer is less than 0.5, the swollen micelles can be much smaller, with larger curvatures, than the inverse swollen micelles, which must confine the longer A blocks on the interior of the curved interface.

The details of the curvature will depend on the relative molecular weights of the different polymers. For example, small molecule homopolymers penetrate into the corresponding copolymer block and have the same qualitative effect as a favorable enthalpic interaction. This effect saturates for homopolymer molecular weights that exceed the molecular weight of the corresponding block, however, so the curvature map shown above as Figure 3 is representative of the behavior of block copolymer surfactants added to blends of high molecular weight polymers.

Conclusions

A ternary system consisting of highly immiscible A and C homopolymers and an AB copolymer, where B and C have favorable interactions, was studied using self-consistent mean-field theory. The copolymer was assumed to be asymmetric, with the volume fraction of the B block ranging from 0.2 to 0.4, and the attraction between the B and C repeat units was varied to give values of $\chi_{bc}N_{cb}$ between 0 and -6. The copolymer segregates to the interface between the immiscible A and C homopolymers, and because the copolymer is asymmetric, it changes the preferred curvature of the interface. When $\chi_{bc} = 0$, the interface curves toward the shorter B block, and swollen micelles form in the A matrix with C homopolymer solubilized in the center of the micelle to accommodate the spontaneous curvature of the interface. If the attraction between B and C is increased by making χ_{bc} negative, the preferred curvature decreases and the radius of the micelle increases in order to maximize the number of B−C contacts as the B block of the copolymer stretches. If the attraction is increased further, the curvature continues to decrease until it crosses zero and becomes negative. At this point inverse swollen micelles form in the C matrix, with A homopolymer solubilized in the center of the micelles to accommodate the negative curvature. The same effect can be achieved by holding χ_{bc} at a constant negative value and increasing f_b. The overall results are presented as an interfacial curvature map that can be used to guide the design of emulsified phases.

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