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BLOCK COPOLYMER AGGREGATES IN MIXTURES OF IMMISCIBLE SOLVENTS

by

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ABSTRACT

Block copolymers act as surfactants in mixtures of two immiscible, inversely selective solvents. The copolymer aggregates at the liquid-liquid interface, leading to the formation of stable microemulsion droplets. Scaling arguments are employed to evaluate the free energy of a single, spherical diblock copolymer aggregate by accounting for the dependence of monomer density on radial distance. The aggregation number and interface curvature are found to be a strong function of the core block molecular weight, and only to a lesser degree of the interfacial tension.

INTRODUCTION

Diblock copolymers in a mixture of two immiscible and selective solvents aggregate at the liquid-liquid interface, thereby causing the formation of stable emulsions. The shape and size of the microemulsion domains are a function of the copolymer composition and the quality of each of the solvents for their respective blocks. Models analyzing such systems¹⁻² have assumed that the monomer volume fraction is uniform throughout the polymer layer. This assumption is

inappropriate for highly curved interfaces, such as in spherical aggregates, where the interface curvature is comparable to the length of the polymer chains so that the volume available to the chains is a strong function of the distance from the interface.

In this study we employ scaling models to analyze the properties of spherical polymeric microemulsion droplets. We use models developed for star polymers and copolymer micelles³⁻⁶, where the dependence of monomer volume fraction on the radius is calculated using geometrical considerations.

SCALING MODEL FOR A SPHERICAL AGGREGATE

We consider the properties of a microemulsion droplet of monodisperse AB diblock copolymer in a mixture of two highly selective and immiscible solvents. The two solvents are assumed to be equally good for their respective blocks. We study a single, spherical aggregate, leaving for further analysis the study of a system of mixed aggregates and free chains. The aggregate consists of three spherically concentric regions: Core (B block), interface, and corona (A block), as depicted in Fig. 1. The copolymer is composed of N_A A segments and N_B B segments. It is assumed that $N_A \gg N_B$, and that the interface between core and corona is sharp so that the copolymer junction points are restricted to a plane. Both blocks are effectively tethered to this plane, forming a brush on both sides of the interface.

In scaling models, a polymer chain is divided into 'blobs' of a characteristic size ξ^7 (see Fig. 1), the excluded volume correlation length. On length scales smaller than ξ excluded volume interactions dominate, but are screened over distances larger than the correlation length. The blobs are assumed to be space filling, so that ξ can be calculated from geometrical considerations. Daoud and Cotton³, and Birshtein and Zhulina⁴, have shown that in dense spherical systems the blob size varies as:

$$\xi(r) \sim \frac{r}{\sqrt{f}} \quad (1)$$

ξ is the blob radius, r is the radial distance and f is the number of chains. The local monomer volume fraction is equal to the volume of the monomers in a blob divided by the volume of a blob, and is therefore a function of r :

$$\phi(r) \sim g \left(\frac{a}{\xi} \right)^3 \sim f^{2/3} \left(\frac{a}{r} \right)^{4/3} \quad (2)$$

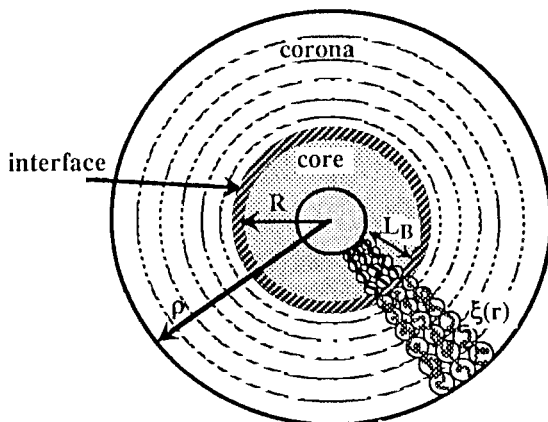


Figure 1. The structure of a spherical aggregate formed by diblock copolymers in a mixture of two immiscible, inversely selective solvents. The aggregate is composed of a core of thickness L_B , an interface with radius R , and a corona with thickness L_A . The total radius of the aggregate is ρ . ξ is the blob size, or excluded volume correlation length.

g is the number of monomers in a blob, proportional to $(\xi/a)^{-5/3}$. a is a segment size scale. The number of blobs in a system is equal to the volume of the polymer shell divided by the volume of a blob:

$$n_{\text{blob}} \sim \int_V \left(\frac{1}{\xi^3} \right) dV \sim f^{3/2} (\ln R_{\text{out}} - \ln R_{\text{in}}) \quad (3)$$

V denotes the volume of a shell between $r=R_{\text{out}}$ and $r=R_{\text{in}}$. Each blob contributes kT 's worth of energy to the system free energy⁷. In order to relate R_{in} and R_{out} , we can use a 'monomer mass balance' since the volume of monomers in a shell is equal to the sum of monomer volume fraction:

$$fNa^3 = \int_V \phi(r) dV \sim f^{2/3} a^{4/3} (R_{\text{out}}^{5/3} - R_{\text{in}}^{5/3}) \quad (4)$$

N is the number of monomers per chain.

We examine the free energy of a microemulsion droplet, assuming that the aggregation number is large enough to justify the use of the Daoud-Cotton analysis leading to Equation 1. The radially dependent monomer volume fraction derived in

Equation 2 replaces the uniform monomer distribution assumed in previous microemulsion models¹⁻². Furthermore, we expect our analysis of a single aggregate to be reasonable at copolymer concentrations that are much higher than the critical aggregation concentration ($c_{\text{polymer}} \gg \text{cmc}$) and at aggregate concentrations that are much lower than the concentration at which aggregates begin to interact significantly ($c_{\text{agg}} \ll c^*_{\text{agg}}$).

The free energy of a spherical microemulsion droplet is composed of a sum of three contributions, respective to the interface, corona and core regions:

$$F_{\text{aggregate}} = F_{\text{interface}} + F_{\text{corona}} + F_{\text{core}} \quad (5)$$

The interface contribution is proportional to the interfacial tension (γ) and the surface area:

$$\frac{F_{\text{interface}}}{kT} \sim \gamma R^2 \quad (6)$$

To calculate the corona contribution, we assume that the overall aggregate size is much larger than the core radius. From Equation 4 R_{out} can be approximated as $N_A^{3/5} f^{1/5}$. From Equation 5 the number of blobs scales as $f^{3/2} \ln(N_A^{3/5} f^{1/5})$. Neglecting the logarithmic term:

$$\frac{F_{\text{corona}}}{kT} \sim f^{3/2} \quad (7)$$

These assumptions are reasonable when $N_A \gg N_B$. The corona contribution is identical to that of a corona in a block copolymer micelle⁵⁻⁶.

Similar simplification can not be made when calculating the core contribution. It is likely that most of the core is essentially filled with a solution of B monomers, so that R and L_B are of the same order of magnitude. The core thickness can be calculated from Equation 4, where $R_{\text{out}} = R$ and $R_{\text{in}} = R - L_B$:

$$L_B \sim R \left\{ 1 - \left(1 - N_B f^{1/3} \left(\frac{a}{R} \right)^{5/3} \right)^{3/5} \right\} \quad (8)$$

And the free energy, using Equation 3:

$$\frac{F_{\text{core}}}{kT} \sim - f^{3/2} \ln \left(1 - N_B f^{1/3} \left(\frac{a}{R} \right)^{3/5} \right) \quad (9)$$

This result resembles the free energy of chains grafted on a flat interface, where (fa^2/R^2) is equivalent to σ , the dimensionless grafting density⁸⁻⁹.

Minimizing the aggregate free energy (Equation 5) with respect to the aggregation number and the interface curvature yields the dependence of the equilibrium aggregate properties on copolymer composition, block molecular weight and the interfacial tension:

$$f \sim N_B^{12/11} (a^2\gamma)^{10/11} \quad (10)$$

$$R \sim a N_B^{9/11} (a^2\gamma)^{2/11} \quad (11)$$

Using these to evaluate the core thickness, we find that $L_B \sim R$. This means that the core is filled with a B in β solution, and there is no 'pure solvent' region in the core. The overall radius of the aggregate (ρ) can be calculated by substituting $N=N_A+N_B$ into Equation 4. Assuming that $N_A \gg N_B$:

$$\rho \sim a \left(\frac{N_A}{N_B}\right)^{3/5} N_B^{9/11} (a^2\gamma)^{2/11} \quad (12)$$

DISCUSSION

We applied a scaling model to systems of diblock copolymers in mixtures of highly selective solvents where microemulsion droplets are formed, emphasizing curvature effects on system properties. We find that the aggregation number and interface curvature are independent of the corona block molecular weight, both an almost linear function of the core block size. In comparison, the core radius of diblock copolymer micelles scales as $N_B^{3/5}$, and the aggregation number as $(N_B^{4/5})^{5-6}$. It is obvious that the microemulsion aggregates are larger, at equal block molecular weight and interfacial tension, than the micelles. A less obvious conclusion of this analysis is that, owing to the stretching of the core block in the microemulsion droplet, the size of these aggregates is a stronger function of the core molecular weight.

Our analysis predicts that both aggregation number and interfacial curvature are independent of the corona block size. This result differs from predictions of a numerical calculations made by Nagarajan and Ganesh². The aggregation number and interface curvature were found to decrease with the corona molecular weight: $f \sim N_A^{-0.39}$, and $R \sim N_A^{-0.13}$. The Nagarajan and Ganesh model is based on the assumption that the monomer density is uniform throughout both core and corona, as in chains tethered to a flat interface. This assumption seems inappropriate when

the core is much smaller than the corona so that the corona structure resembles a star. In such a case, the corona chains are only slightly deformed from their free chain dimensions and their effect on the aggregation number and interface curvature is negligible. Data are needed to examine this idea.

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