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Solubilization in spherical block copolymer micelles: Scaling analysis based on star model

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We develop a theory of solubilization of low molecular weight species in block copolymer micelles, employing the scaling approach and building on the analogy between micelles and star polymers. Specifically, we consider spherical micelles of AB-diblock copolymers formed in selective solvents, in which the core and the shell regions are assumed to have radial concentration variations similar to those occurring in the solution state of a star polymer. Invoking the results for the conformation of a star polymer derived by Daoud and Cotton, expressions are developed for the free energy per molecule of the micelle ΔG, the core radius R, the shell thickness D, and the overall volume fraction of the polymer within the core ϕ_A as functions of the micellar aggregation number g. From the minimization of the free energy of an isolated micelle, the equilibrium values for all the micellar structural parameters and for the extent of solubilization are obtained. The results expressed as scaling relations for g, R, D, and ϕ_A are derived for various situations of interest including those of the solvent S being a good or theta solvent for the shell block B, and the solubilizate J being a good or theta solvent for the core block A.

I. INTRODUCTION

AB diblock copolymer molecules present in solvent S, which is selective for one of the blocks (say, B), spontaneously self-assemble to form micellar aggregates.[1,2] In these micelles, one can identify a core region made up of the solvophobic A block surrounded by a shell region made up of the solvophilic B block and the solvent S. The solvophobic core provides a microenvironment capable of accommodating other species J that are characterized by their negligible solubility in solvent S. In this manner, the effective solubility of J is dramatically enhanced by the presence of micelles, compared to the solubility of J in the micelle-free solvent S. This phenomenon, known as solubilization, is responsible for many practical applications of block copolymers as polymeric surfactants. For example, our experiments have demonstrated that block copolymer micelles in water exhibit selective solubilization, such as preferring aromatic hydrocarbons compared to aliphatic hydrocarbons.[3] Such selectivity in solubilization can be exploited as the basis of novel separation processes, say, for the extraction of drug molecules from plants. We have shown that a variety of flavor compounds can be solubilized in aqueous solutions of block copolymer micelles to prepare stable, uniform, and easy-to-handle liquid flavorings for use in the food and beverage industries.[4] We have also demonstrated the feasibility of solubilizing enzymes along with controlled amounts of water in block copolymer micelles formed in nonpolar solvents in order to carry out biocatalytic reactions involving water-insoluble reactants and products.[5]

The solubilization capacity of the micelle and its other microscopic features can be expected to depend on the type of molecular interactions involving blocks A and B, the solvent S, and the solubilizate J as well as on the molecular sizes of all the species. In general, the solvent S may be a theta solvent or a good solvent for the B block. The solubilizate J which is virtually immiscible with S may be a theta solvent or a good solvent for the A block. One may anticipate intuitively that the nature of A–J interactions would be a key factor influencing the capacity of the micelles for the solubilizate J. Experimental measurements[3,4] show that the ratio of the volume of solubilizate J to the volume of the A block in the micelles varies between 0 and approximately 1, the largest ratio being realized when J is a good solvent for the A block.

To predict the solubilization behavior of block copolymer micelles, we recently developed a mean-field theory focusing on AB-diblock copolymers.[6] In this theory, the micelles were assumed to be spherical in shape. Two closely related structures which are used to describe solubilization [Fig. 1(a)] and microemulsions [Fig. 1(b)] in the literature dealing with conventional surfactants were considered. In the more general structure shown in Fig. 1(b), the micellar core contains a pool of pure solubilizate J in the interior surrounded by a region where the solubilizate J and the solvophobic A block are both present. The shell region of the micelle is made up of the solvophilic B block and the solvent S. This structure reduces to that shown in Fig. 1(a) when the radius of the solubilizate pool decreases to zero. Assuming that concentrations are uniform in all the regions of the micelle, we used a Flory-type mean-field approach to quantify the free energy of formation of micelles containing the solubilizate. From the minimization of the free energy per molecule of the micelle, all the equilibrium characteristics of the micelles such as the aggregation number g, the core radius R, the shell thickness D, the radius of the solubilizate pool R_p, and the vol-
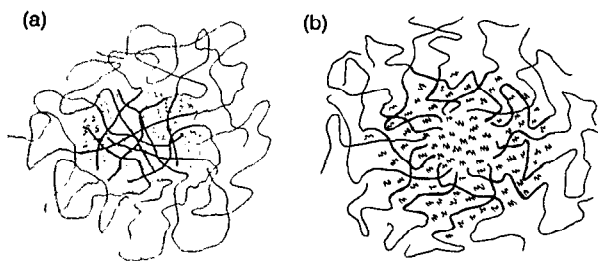

FIG. 1. A schematic representation of a spherical micelle containing the solubilizate. The darker lines denote the solvophobic A block, while the lighter lines refer to the solvophilic B block. The solvent S, not shown in the figure, penetrates the shell region of the micelle. (a) In this mode of solubilization, the micellar core consists of a solution of solubilizate J with the A block. (b) In this mode of solubilization, the micellar core consists of a solubilizate pool in the interior surrounded by a region where solubilizate J is present as a solution with the A block.

ume fraction of the solubilizate in the core η were calculated. Also, the critical micelle concentration (CMC) was determined knowing the magnitude of the free energy of micelle formation. Inevitably, all the above results had to be obtained based on detailed numerical calculations. To make accessible our theory for use by others, the extensive numerical results were fitted to empirical equations that correlated the microscopic features of the micelles to the molecular properties of all the constituent species. For the wide range of copolymer, solvent, and solubilizate properties explored in this study, the theory predicted that the radius of the solubilizate pool in the equilibrium aggregate structure is zero, implying that Fig. 1(a) depicts the preferred equilibrium structure.

The assumption that the core and the shell regions are at uniform concentrations, made in our mean-field theory described above, constitutes one idealization of the micelle. An alternate idealization would be to allow for concentration inhomogeneities to exist in both these regions as, e.g., radial concentration variations in spherical micelles consistent with the aggregate shape. Different approaches may be followed to develop a theory of solubilization, which incorporates such concentration inhomogeneities in the micelle. In this paper, we build our theory by relying on the analogy between the conformation of star-shaped polymers and spherical micelles, hence the title of the paper, star model.

Star polymers resemble spherical micelles, but for the important difference that a chemical link exists at the center between the various branches of the star polymer. Daoud and Cotton[7] studied the conformation of a uniform star polymer, with g branches joining at the origin, present in a good solvent. They identified three distinct regions in this conformation. For each of these three regions, they developed expressions for the radial concentration profiles utilizing the concept of blobs employed in theories of semidilute solutions of linear polymers. They also derived an expression for the spatial extension of the branches as a function of the number of branches in the star polymer. In this paper, we utilize the Daoud–Cotton analysis to obtain the radial concentration variations in the core and the shell regions of the micelle as well as to develop expressions for

the free energy of micellization and solubilization.

The star model of solubilization formulated in this paper uses the scaling approach.[8] This allows us to obtain scaling relations for the equilibrium properties of the micelles in many interesting situations without having to perform extensive numerical computations of the type required by our earlier mean-field theory. As is conventional in scaling analysis, we will ignore all numerical coefficients while writing various equations. Furthermore, all the spatial variables such as the core radius R, the shell thickness D, the core area per molecule a, and the interfacial thickness τ appearing in the analysis are expressed as dimensionless quantities. For simplicity, the molecular sizes of the solvent S, the solubilizate J, the segment of the A block, and the segment of the B block are all assumed to be equal. This characteristic size is used as the unit to represent all the dimensionless spatial variables. Also, the energy variables such as the free energy of aggregation ΔG and the interfacial tension γ are expressed in units of kT, where k is the Boltzmann's constant and T is the absolute temperature. We develop an expression for the free energy (per molecule) of the micelle containing the solubilizate, using the blob visualization intrinsic to the star model. From the minimization of this free energy, all the equilibrium characteristics of the micelle are determined. We have already shown how such an approach based on the minimization of the free energy of an isolated micelle, known as the pseudophase model in the literature, provides results virtually identical to that obtained from a detailed calculation of the size and the composition distribution of micelles.[6] We have also discussed how the critical micelle concentration can be estimated knowing the free energy of micelle formation. In this paper, we will not review these aspects again, but instead focus entirely on developing scaling relations for the equilibrium structure of a spherical micelle containing the solubilizate. The present theory can readily be extended to cylindrical and lamellar aggregates as well.

The scaling analysis and the star model have been used before to describe block copolymer micelles. The pioneering work is that of de Gennes[9] who carried out a scaling analysis of both spherical and lamellar aggregates. A scaling analysis of spherical and cylindrical micelles in good and theta solvents, based on the star model, has been developed by Zhulina and Birshtein.[10] The star model for spherical micelles in good solvents has been independently formulated, also by Halperin.[11] Recently, a scaling analysis of diblock copolymer microemulsions based on the star model has been developed by Dan and Tirrell[12] for the situation when the solubilizate J is a good solvent for the A block, and solvent S is a good solvent for the B block. This corresponds to one of the cases considered in the present paper. Dan and Tirrell assume that the spherical microemulsion droplets include a solubilizate pool in their interiors, as shown in Fig. 1(b). Their model predicts that the ratio of the volume of solubilizate to the volume of the solvophobic A block is typically much larger than unity. As mentioned earlier, the experimentally observed solubilization capacities of micelles are relatively smaller. Also, our mean-field theory[6] predicted that a solubilizate pool is

not present in the micelle core. Hence, we assume in our present work that the radius of the solubilizate pool in the core is zero as shown in Fig. 1(a). One may note that the presence or absence of the solubilizate pool in the structural description of the spherical micelle does not affect the scaling relations, since only various limiting situations are considered while deriving the scaling relations. Consequently, the scaling relations derived by Dan and Tirrell are in agreement with our results for the case when the solvent S and the solubilizate J are good solvents for the B block and the A block, respectively. Besides spherical structures, Dan and Tirrell[12] have also examined the occurrence of cylindrical and lamellar structures in microemulsion systems and have presented scaling relations for these shapes as well.

While the present paper focuses on small molecular weight solvents and solubilizates, a complementary system is one in which the solvent and solubilizate are both homopolymers of large molecular weight. Such a system has recently been analyzed by Wang and Safran.[13] They have also treated the problem of block copolymer monolayers where one block is of uniform density, while the other block is swollen by a solvent.[14]

In the following section, the Daoud and Cotton model for the conformation of a star polymer is briefly recapitulated. In Sec. III, expressions for the free energy of solubilization in block copolymer micelles are formulated. In Sec. IV, scaling results are derived for the micellar structural parameters for various situations of interest. The last section presents the conclusions from this work.

II. MODEL OF THE STAR POLYMER—RECAPITULATION

Daoud and Cotton[7] have examined the conformation of a uniform star polymer containing g branches, with N statistical units in each branch, present in a good solvent. Three important concepts are introduced as part of their analysis. First, the local concentration ϕ of the statistical units is assumed to be a function of the radial distance r from the center of the star. Second, a branch of the star is assumed to have locally a single free-chain behavior within a blob of size ξ analogous to the case of linear polymers. The blob size ξ is also dependent on the radial position r at which the blob is located. Third, all the branches of the star are considered to diffuse outwards in such a way that all the g branches are present in any spherical region located at a distance r and contribute equally to the concentration of the segments in that region. Knowing the radial concentration profile $\phi(r)$ and the blob size $\xi(r)$, the spatial extension of the branches and the free energy of the star polymer can be calculated.

In determining $\phi(r)$ and $\xi(r)$, Daoud and Cotton identified three regions in the conformation of a star polymer—a swollen region, an unswollen region, and a uniform density region. Their main results for each of these regions relevant to our present theory are summarized below.

A. Swollen region

At a large distance from the center of the star, each branch of the star polymer can be expected to behave as an independent free chain since the branches are far apart from one another. Therefore, blobs of size $\xi(r)$ containing $n(r)$ segments are swollen in this region. The local swelling parameter $\alpha(r)$ has a dependence on $n(r)$ as for single linear chains, namely,

$$\alpha(r)^5 = \omega n(r)^{1/2}. \tag{1}$$

Here, $\omega = \frac{1}{2} - \chi$ is the excluded volume parameter, χ being the Flory interaction parameter. We use the equality sign in Eq. (1) and the various equations below with the understanding that numerical coefficients have been ignored in all the equations, in the context of a scaling analysis. Considering that the unperturbed dimension of $n(r)$ segments is $n(r)^{1/2}$, the blob size and the concentration of segments within it are given by

$$\xi(r) = \alpha(r)n(r)^{1/2}, \quad \phi(r) = \frac{n(r)}{\xi(r)^3}. \tag{2}$$

To determine the four unknowns $n(r)$, $\alpha(r)$, $\phi(r)$, and $\xi(r)$ appearing in the above equations, one makes use of the assumption that all the branches of the star contribute equally to the segment concentration at any radial distance r. Since, $gn(r)$ segments are present in a spherical shell of volume $r^2\,\xi(r)$ located at r, one gets

$$\phi(r) = \frac{gn(r)}{r^2\xi(r)}. \tag{3}$$

Combining Eqs. (1)–(3) all the variables can be determined

$$n(r) = r^{5/3}g^{-5/6}\omega^{-1/3}, \quad \alpha(r) = r^{1/6}g^{-1/12}\omega^{1/6},$$
$$\xi(r) = rg^{-1/2}, \quad \phi(r) = r^{-4/3}g^{2/3}\omega^{-1/3}. \tag{4}$$

As one would expect, $\alpha(r)$ and $\xi(r)$ are increasing functions of r, while $\phi(r)$ is a decreasing function of r.

B. Unswollen region

As one moves towards shorter distances from the center of the star compared to the previous case, $\alpha(r)$ decreases and eventually at $r = r_1$ assumes a value of unity. By equating $\alpha(r)$ in Eq. (4) to unity, we determine r_1 to be

$$r_1 = g^{1/2}\omega^{-1}. \tag{5}$$

For radial distances r less than r_1, the blobs are not swollen. Thus,

$$\alpha(r) = 1, \quad \xi(r) = n(r)^{1/2}. \tag{6}$$

The segment concentration $\phi(r)$ is described by Eqs. (2) and (3) as before. Combining Eqs. (2), (3), and (6), all the variables get determined. Thus we obtain

$$n(r) = r^2g^{-1}, \quad \xi(r) = rg^{-1/2}, \quad \phi(r) = r^{-1}g^{1/2}. \tag{7}$$

C. Uniform density region

As one moves towards yet shorter distances from the center of the star, the segment concentration continues to increase, reaching the limiting value of unity at $r=r_2$. The magnitude of r_2 is determined by equating $\phi(r)$ in Eq. (7) to unity

$$r_2=g^{1/2}, \quad \phi(r)=1. \tag{8}$$

For radial distances $r<r_2$, the polymer segments are in the melt state and the blob visualization is not employed in this region.

Having defined $\xi(r)$ and $\phi(r)$ in all the three regions, one can calculate the extension L of the branches as well as the free energy of the star polymer. The magnitude of L is obtained from the mass conservation relation

$$Ng= \int_0^L r^2\phi(r)dr. \tag{9}$$

The free energy of the star polymer in the swollen and the unswollen regions accounts for both the stretching of polymer segments and their mixing with the solvent. This free energy is simply equal to the total number of blobs in the two regions. In the uniform density region of radius r_2, the polymer is in the melt condition and the free energy is estimated by considering simply the stretching of the chains over the length r_2. Within this region, each branch of the star polymer has (r_2^3/g) segments, since all the branches are assumed to contribute equally to the segment densities at any position. Therefore, the free energy per branch of the star polymer is obtainable from

$$\Delta G=\frac{r_2^2}{(r_2^3/g)}+\frac{1}{g} \int_{r_2}^L \frac{r^2\,dr}{\xi(r)^3}. \tag{10}$$

Here, the first term describes the stretching free energy of the chains in the uniform density region, while the second term calculates the total number of blobs in the unswollen and the swollen regions.

In the following treatment of solubilization, $\phi(r)$ and $\xi(r)$ in the micellar core and the shell regions are taken to be analogous to those for a star polymer. We then use Eq. (9) to obtain the dependence of the core radius R, the shell thickness D, and the overall volume fraction of A segments within the core ϕ_A on the micelle aggregation number g. Furthermore, we use Eq. (10) to calculate the components of the free energy of solubilization as functions of g.

III. FREE ENERGY OF SOLUBILIZATION

Our earlier mean-field theory of solubilization,[6] which accounted for both the size and the composition distribution of micelles, predicted that the micellar aggregation number and the volume fraction of the solubilizate within the core of the micelles are both very narrowly dispersed about their mean values. Therefore, in the present work, we do not consider the size and the composition distribution of micelles, but only micelles of a single size having the same volume fraction of the solubilizate in the core of the micelle. Furthermore, given the validity of the pseudophase model for treating micellar systems and the

resulting simplicity of analysis, we concentrate on an isolated micelle rather than on the entire micellar solution. We consider a spherical micelle made of g block copolymer molecules. The block copolymer has N_A segments in the solvent-incompatible A block and N_B segments in the solvent-compatible B block. Both N_A and N_B are appreciably large compared to unity. The core region of the micelle is composed only of the A segments and the solubilizate J. The segments of the B block and the solvent S which are entirely excluded from the micellar core are present in the shell region of the micelle. The core radius is denoted by R and the shell thickness is denoted by D. The overall volume fraction of the A segments within the core region is denoted by ϕ_A,

$$\phi_A=\frac{gN_A}{R^3}. \tag{11}$$

The volume fraction of the solubilizate within the micellar core η is thus given by $(1-\phi_A)$. Obviously, ϕ_A is equal to unity in the absence of solubilizate. We can express the core radius R as a function of the aggregation number g from Eq. (11)

$$R=N_A^{1/3}g^{1/3}\phi_A^{-1/3}. \tag{12}$$

The surface area of the core per block copolymer molecule is denoted by a and it is related to the aggregation number g via the expression

$$a=\frac{R^2}{g}=N_A^{2/3}g^{-1/3}\phi_A^{-2/3}. \tag{13}$$

The free energy of an isolated micelle per molecule of the constituent block copolymer (with respect to some reference state) is denoted by ΔG. ΔG depends on the micellar structural parameters g, R, ϕ_A, and D and has a minimum when these parameters assume their equilibrium values. It is the knowledge of this dependence of ΔG on the structural parameters that is essential for predicting the properties of the equilibrium micelle. If ΔG includes contributions that are only weakly dependent on the structural parameters, then these contributions may be treated as constants. It is not necessary to know precisely these constant terms for determining the micellar size parameters. In contrast, the estimation of the critical micelle concentration requires knowledge of the actual magnitude of the free energy of the micelle with respect to the reference state of an isolated block copolymer molecule in solution. Therefore, for the calculation of the CMC, it is necessary to know precisely even the constant terms contributing to ΔG.

The free energy of formation of the micelle is composed of four parts

$$\Delta G=\Delta G_A+\Delta G_B+\Delta G_I+\Delta G_L. \tag{14}$$

The contribution ΔG_A refers to the change in state of the A blocks following micellization and solubilization. ΔG_B represents a corresponding contribution from the B blocks. ΔG_I denotes the free energy of formation of an interface between the core and the shell regions of the micelle. The contribution ΔG_L accounts for the localization of the A–B

link of the copolymer at the micellar interface. As will be seen below, ΔG_L is practically a constant and therefore not important for determining the structure of the equilibrium micelle. We develop below expressions for each of the abovementioned free energy contributions as a function of g for various cases of interest.

A. Estimation of ΔG_A

We estimate this free energy contribution for three situations: (a) uniform density core; (b) unswollen core; and (c) swollen core. The conditions characterizing their occurrence and the corresponding free energy contributions are discussed here.

1. Uniform density core

In this case, the micellar core consists of only one of the three regions identified in a star polymer, namely, that of uniform density. Obviously, such a situation arises when there is no solubilizate. Thus this case describes micellization in the absence of solubilizates. For this condition, Eq. (12) reduces to

$$\phi_A = 1, \quad R = N_A^{1/3} g^{1/3} \tag{15}$$

The free energy contribution ΔG_A arises from the stretching of the A chains on micelle formation and is calculated from the first term of Eq. (10). Noting that $r_2 = R$ and $r_2^3/g = N_A$, we get

$$\Delta G_A = \frac{r_2^2}{(r_2^3/g)} = \frac{R^2}{N_A} = N_A^{-1/3} g^{2/3}. \tag{16}$$

2. Unswollen core

In star polymers, if an unswollen region occurs, then of necessity a uniform density region must also be present towards the center of the star because of the chemical link at the center between the various branches of the star. In micelles, no such link between the various constituent molecules exists at the center of the micelle. Therefore, it is conceivable that the entire micellar core is characterized by an unswollen region and a uniform density region may not be present at all. No theoretical calculation of density profiles in such systems is presently available. However, experimental studies on conventional surfactant micelles show[15] that depending on the type and the amount of solubilization, the solubilizate molecules may be located mainly in the outer regions of a spherical micellar core, leaving the interior to be a uniform density region. If the block copolymer micelles behave similar to such conventional surfactant micelles, then their core may consist of both unswollen and uniform density regions.

We will adopt the most general visualization and consider that the micellar core consists of two of the three regions identified in a star polymer, namely, the uniform density region and the unswollen region, the latter being the dominant part of the core for the purposes of scaling analysis. This case occurs (i) when the solubilizate J is a theta solvent for the A block, i.e., $\chi_{AJ} = \frac{1}{2}$, or (ii) if the solubilizate J is a good solvent for the A block, but N_A is not sufficiently large. We can determine the micellar core

radius R as a function of g by applying Eq. (9) over the uniform density and the unswollen regions of the core. The local volume fractions of the A segments in the two regions are given by Eqs. (8) and (7), respectively,

$$N_A g = \int_0^{r_2} r^2(1) dr + \int_{r_2}^R r^2(r^{-1} g^{1/2}) dr, \tag{17}$$

where r_2 is given by Eq. (8). Since the unswollen region is the dominant part of the core (implying R is much larger than r_2), we obtain from the above equation

$$R = N_A^{1/2} g^{1/4}, \quad \phi_A = \frac{N_A g}{R^3} = N_A^{-1/2} g^{1/4}. \tag{18}$$

The free energy contribution ΔG_A is computed from Eq. (10), after introducing Eq. (7) for the blob size

$$\Delta G_A = \frac{r_2^2}{(r_2^3/g)} + \frac{1}{g} \left[\int_{r_2}^R \frac{r^2 \, dr}{(rg^{-1/2})^3} \right]$$

$$= g^{1/2} \left(1 + \ln \frac{R}{g^{1/2}} \right) = g^{1/2} K_A. \tag{19}$$

In Eq. (19), the term appearing within the brackets is denoted by K_A. We note that this term has only a weak dependence on the micellar structural parameters because of the logarithmic functionality. Therefore, in the spirit of scaling analysis, we will consider K_A to be a constant while taking the derivative of ΔG with respect to g.

3. Swollen core

In star polymers, the occurrence of a swollen region implies the existence of uniform density and unswollen regions towards the center of the star because of the connectivity of the branches. As discussed in the previous case, all three regions need not exist in the micellar core because the molecules constituting the micelle are not linked at the center. We adopt, however, the most general picture and consider that the micellar core consists of all three regions identified in a star polymer, with the swollen region being the dominant part of the micelle core for the purposes of the scaling analysis. This situation occurs when the solubilizate J is a good solvent for the A block and at the same time N_A is sufficiently large. The core radius R of the micelle is determined from Eq. (9) applied over all three regions of the core, where the local volume fractions of the A segments are given by Eqs. (4), (7), and (8), respectively,

$$N_A g = \int_0^{r_2} r^2(1) dr + \int_{r_2}^{r_1} r^2(r^{-1} g^{1/2}) dr$$

$$+ \int_{r_1}^R r^2(r^{-4/3} g^{2/3} \omega_A^{-1/3}) dr. \tag{20}$$

Here, r_1 is given by Eq. (5) and r_2 is given by Eq. (8). The excluded volume parameter ω is now $\omega_A = \frac{1}{2} - \chi_{AJ}$, χ_{AJ} being the Flory interaction parameter between the A segments and the solubilizate J. Since the swollen region is the

dominant part of the core (implying R is much larger than r_1), the above equation can be simplified by ignoring the first two terms. Thus,

$$R = N_A^{3/5} g^{1/5} \omega_A^{1/5}, \quad \phi_A = \frac{N_A g}{R^3} = N_A^{-4/5} g^{2/5} \omega_A^{-3/5}. \quad (21)$$

The free energy contribution ΔG_A which accounts for the deformation of the A chains as well as their swelling by the solubilizate J can be calculated from Eq. (10) incorporating Eqs. (4) and (7) for the blob sizes. One obtains

$$\Delta G_A = \frac{r_2^2}{(r_2^3/g)} + \frac{1}{g} \left[\int_{r_2}^{r_1} \frac{r^2\, dr}{(rg^{-1/2})^3} + \int_{r_1}^{R} \frac{r^2\, dr}{(rg^{-1/2})^3} \right]$$

$$= g^{1/2} \left(1 + \ln \frac{R}{g^{1/2}} \right) = g^{1/2} K_A. \quad (22)$$

As mentioned before, since K_A is a logarithmic function, it will be treated as a constant while taking the derivative of ΔG with respect to g.

B. Estimation of ΔG_B

The free energy contribution ΔG_B arises from the enhanced concentration of the B segments in the micellar shell region compared to the free B coils in solution. We estimate this contribution in two situations: (a) unswollen shell and (b) swollen shell. The conditions for the occurrence of these two situations and the corresponding free energy contributions ΔG_B are discussed here.

1. Unswollen shell

This case describes a micellar shell which is analogous to the unswollen region of a star polymer. This situation arises (i) when the solvent S is a theta solvent for the B block, i.e., $\chi_{BS} = \frac{1}{2}$, or (ii) when the solvent S is a good solvent for the B block, but both N_A and N_B are not sufficiently large. The shell thickness D is determined by applying Eq. (9) over the unswollen region where the local volume fraction of the B segments is given by Eq. (7)

$$N_B g = \int_R^{R+D} r^2 (r^{-1} g^{1/2})\, dr. \quad (23)$$

Therefore,

$$D = N_B^{1/2} g^{1/4} \left(\text{for } \frac{D}{R} \gg 1 \right),$$

$$D = N_B g^{1/2} R^{-1} \left(\text{for } \frac{D}{R} \ll 1 \right). \quad (24)$$

The free energy contribution is obtained from Eq. (10) applied over the unswollen region, where the blob size is represented by Eq. (7)

$$\Delta G_B = \frac{1}{g} \left[\int_R^{R+D} \frac{r^2\, dr}{(rg^{-1/2})^3} \right]$$

$$= g^{1/2} \ln \left(1 + \frac{D}{R} \right) = g^{1/2} K_B. \quad (25)$$

In the above equation, we have denoted the logarithmic factor by K_B. Analogous to the treatment of K_A, the factor K_B is also considered to be a constant while taking the derivative of ΔG with respect to g.

2. Swollen shell

In this case, the micellar shell is analogous to the swollen region of a star polymer. This situation arises (i) when the solvent S is a good solvent for the B block and N_B is sufficiently large, or (ii) when the solvent S is a good solvent for the B block and N_B is small, but N_A is sufficiently large. The shell thickness D is calculated from Eq. (9), in conjunction with Eq. (4) applied to the swollen region.

$$N_B g = \int_R^{R+D} r^2 (r^{-4/3} g^{2/3} \omega_B^{-1/3})\, dr, \quad (26)$$

where $\omega_B = \frac{1}{2} - \chi_{BS}$ is the excluded volume parameter for the B block in solvent S. The above equation yields

$$D = N_B^{3/5} g^{1/5} \omega_B^{1/5} \left(\text{for } \frac{D}{R} \gg 1 \right),$$

$$D = N_B g^{1/3} \omega_B^{1/3} R^{-2/3} \left(\text{for } \frac{D}{R} \ll 1 \right). \quad (27)$$

The free energy contribution ΔG_B is determined from Eqs. (4) and (10) applied to the swollen region

$$\Delta G_B = \frac{1}{g} \left[\int_R^{R+D} \frac{r^2\, dr}{(rg^{-1/2})^3} \right]$$

$$= g^{1/2} \ln \left(1 + \frac{D}{R} \right) = g^{1/2} K_B, \quad (28)$$

where K_B is treated as a constant, while taking the derivative of ΔG with respect to g.

C. Estimation of ΔG_I

This contribution accounts for the formation of an interface between the micellar core and the micellar shell. It can be written as the product of the core surface area per molecule a and an interfacial tension γ that is characteristic of this interface. We consider the two limiting situations (a) solubilizate-free core and (b) solubilizate-containing core.

1. Solubilizate-free core

Obviously, this case describes micelle formation in the absence of solubilizate. Correspondingly, the micellar interface is that between a pure A polymer on the core side and a solution of the B polymer in solvent S on the shell side. The characteristic interfacial tension γ will be some composite of the polymer A–polymer B interfacial tension γ_{AB} and the polymer A–solvent S interfacial tension γ_{AS}. Therefore, in view of Eq. (13) for the area a, we can write

$$\Delta G_I = \gamma a = \gamma N_A^{2/3} g^{-1/3}. \quad (29)$$

2. Solubilizate containing core

In the presence of the solubilizate, the interface is that between a solution of A polymer in solubilizate J on the

core side and a solution of B polymer in solvent S on the shell side. The characteristic interfacial tension γ will be some composite of the four individual interfacial tensions polymer A–polymer B (γ_{AB}), polymer A–solvent S (γ_{AS}), polymer B–solubilizate J (γ_{BJ}), and solubilizate J–solvent S (γ_{JS}). In the analogous case of a free polymer solution, the interfacial tension is found to depend nonlinearly on polymer concentration at very low concentrations because of selective adsorption or depletion effects.[16] At higher polymer concentrations, a linear dependence is observed. However, the micellar interface is not the same as that of a free polymer solution because the A–B link of the copolymer is localized at the interface, forcing other connected segments to remain at the interface irrespective of selective adsorption or depletion effects. Thus an unambiguous estimate for γ is not possible at present and a fundamental treatment for estimating γ at the micellar interface is warranted. Consequently, given the area a from Eq. (13), we can write

$$\Delta G_I = \gamma a = \gamma N_A^{2/3} g^{-1/3} \phi_A^{-2/3}. \tag{30}$$

D. Estimation of ΔG_L

This free energy contribution accounts for a part of the reduction in entropy arising from the structural organization of free molecules into micelles. Specifically, this contribution describes the constraint imposed on the A–B link of the block copolymer to remain at the interface separating the micellar core from the shell because of molecular aggregation. This free energy is estimated here using the concept of a volume restriction model. If the block copolymer molecules were not structurally organized in a micelle, the A–B link of the block copolymer would have translational freedom over the entire volume of the micelle. (Note that the translational freedom of the micelle over the entire system volume is separately considered as the translational entropy in a complete thermodynamic formulation. Hence, the attention is focused on a single micelle here.) However, because of the structural organization of the molecules in a micelle, the translational freedom of the A–B link of the copolymer is localized to a small interfacial volume surrounding the core of the micelle. ΔG_L is estimated on the basis of such a volume restriction model

$$\Delta G_L = \ln \frac{(R+D)^3}{\tau R^2} = K_L, \tag{31}$$

where the numerator within the logarithmic factor denotes the total volume of the micelle, while the denominator represents the volume of a thin interfacial region of thickness τ. When the micellar core and shell regions are very incompatible, such as those of interest to our study, the interfacial thickness is expected to be of the order of the segment length. Hence, the dimensionless thickness τ is of the order of unity. We denote the logarithmic term by K_L and note that because of the logarithmic functionality, it has only a weak dependence on the micellar structural parameters. Therefore, as in the cases of K_A and K_B encountered before, K_L is also treated as a constant, while taking the derivative of ΔG with respect to g. Conse-

quently, the localization free energy contribution has no influence over the equilibrium properties of the micelle. This feature was already observed in our earlier mean-field theory of micellization[17] and of solubilization.[6]

IV. RESULTS FROM THE STAR-MODEL OF SOLUBILIZATION

Expressions for the free energy contributions to ΔG derived in the previous section show that, in general, ΔG_A and ΔG_B are increasing functions of g, while ΔG_I is a decreasing function of g. Thus, the free energy contribution ΔG_I is responsible for the cooperative growth of the micelle, while ΔG_A and ΔG_B serve to restrict the micellar growth to finite sizes. Since the free energy contribution ΔG_L is virtually independent of g, it has no effect on the equilibrium characteristics of the micelle. Below, we obtain the scaling relations for all the structural parameters of the equilibrium micelle corresponding to various cases of interest. For each description of the core and the shell regions, we simply refer to Sec. III and find the needed expressions for R, D, ϕ_A, ΔG_A, ΔG_B, and ΔG_I as functions of the aggregation number g. By minimizing ΔG with respect to g, the equilibrium value for g is obtained. Once g is known, the parameters R, D, and ϕ_A corresponding to the equilibrium micelle can be directly calculated.

A. Micellization—uniform density core and swollen shell

The free energy of the micelle per block copolymer molecule is written incorporating the appropriate contributions derived in the previous section. We get

$$\Delta G = N_A^{-1/3} g^{2/3} + g^{1/2} K_B + \gamma N_A^{2/3} g^{-1/3} + K_L. \tag{32}$$

The analytical minimization of ΔG with respect to g is not possible for the above functional form. Therefore, we carry out such minimization for the two limiting cases when either ΔG_A or ΔG_B is dominant compared to one another.

When N_B is much smaller than N_A, the shell block free energy contribution ΔG_B is negligibly small compared to the core block free energy contribution ΔG_A. One may note that when $N_B \ll N_A$, we have correspondingly $D/R \ll 1$. Neglecting ΔG_B from Eq. (32), the minimization of ΔG with respect to g in conjunction with Eq. (15) yields

$$g = N_A \gamma, \quad R = N_A^{2/3} \gamma^{1/3}. \tag{33}$$

The shell thickness D is obtained from Eq. (27), in which the expressions for g and R from above are introduced

$$D = N_A^{-1/9} N_B \gamma^{1/9} \omega_B^{1/3}. \tag{34}$$

The parameter K_B can be estimated knowing D and R,

$$K_B = \ln \left(1 + \frac{D}{R} \right) = \frac{D}{R} = N_A^{-7/9} N_B \gamma^{-2/9} \omega_B^{1/3}. \tag{35}$$

The condition $\Delta G_A \gg \Delta G_B$ for which the above scaling results are valid can be defined using Eqs. (32)–(35) as

$$N_A \gg N_B^{18/11} \gamma^{-7/11} \omega_B^{6/11}. \tag{36}$$

Alternately, when N_B is much larger than N_A, the core block free energy contribution ΔG_A is much smaller than

the shell block free energy contribution ΔG_B, and hence can be ignored. Also, when $N_B \gg N_A$, $D/R \gg 1$. Neglecting ΔG_A in Eq. (32), the minimization of ΔG with respect to g in conjunction with Eq. (15) leads to

$$g = N_A^{4/5}\gamma^{6/5}K_B^{-6/5}, \quad R = N_A^{3/5}\gamma^{2/5}K_B^{-2/5}. \quad (37)$$

The shell thickness D is obtained by combining Eqs. (27) and (37)

$$D = N_A^{4/25}N_B^{3/5}\gamma^{6/25}\omega_B^{1/5}K_B^{-6/25}. \quad (38)$$

The parameter K_B is estimated from the knowledge of D and R to be

$$K_B = \ln\left(1+\frac{D}{R}\right) = \ln\left(\frac{D}{R}\right)$$

$$= \ln(N_A^{-11/25}N_B^{3/5}\gamma^{-4/25}\omega_B^{1/5}K_B^{4/25})$$

$$= \ln(N_A^{-11/25}N_B^{3/5}), \quad (39)$$

where the last equality is an approximation arrived at by comparing the relative magnitudes of the different variables present in the expression for K_B. The conditions $\Delta G_A \ll \Delta G_B$ and $D/R \gg 1$ are both satisfied when

$$N_A \ll N_B^{15/11}\gamma^{-4/11}\omega_B^{5/11}K_B^{4/11}. \quad (40)$$

The scaling relations (33) were first obtained by de Gennes[8] from his pioneering application of scaling analysis to block copolymer micelles. Scaling relations (37) were derived independently by Zhulina and Birshtein[9] and Halperin[10] from their application of the star model to micelle formation in good solvents.

B. Micellization—uniform density core and unswollen shell

The free energy of the micelle per block copolymer molecule is identical to that given by Eq. (32) for Sec. IV A, but the expressions for the shell thickness D and the parameter K_B are, however, different from those for Sec. IV A. In the limit of $\Delta G_A \gg \Delta G_B$ and $D/R \ll 1$, we get

$$g = N_A\gamma, \quad R = N_A^{2/3}\gamma^{1/3}. \quad (41)$$

The shell thickness is obtained from combining Eqs. (24) and (41)

$$D = N_A^{-1/6}N_B\gamma^{1/6}. \quad (42)$$

Correspondingly, K_B can be estimated as

$$K_B = \ln\left(1+\frac{D}{R}\right) = \frac{D}{R} = N_A^{-5/6}N_B\gamma^{-1/6}. \quad (43)$$

The condition $\Delta G_A \gg \Delta G_B$, $D/R \ll 1$ for which the above scaling relations are valid is satisfied when

$$N_A \gg N_B^{3/2}\gamma^{-1/2}. \quad (44)$$

In the opposite limit of $\Delta G_A \ll \Delta G_B$, $D/R \gg 1$, we have from before

$$g = N_A^{4/5}\gamma^{6/5}K_B^{-6/5}, \quad R = N_A^{3/5}\gamma^{2/5}K_B^{-2/5}. \quad (45)$$

The shell thickness D is calculated from Eqs. (24) and (45) to be

$$D = N_A^{1/5}N_B^{1/2}\gamma^{3/10}K_B^{-3/10}. \quad (46)$$

The parameter K_B can be estimated as

$$K_B = \ln\left(1+\frac{D}{R}\right) = \ln\left(\frac{D}{R}\right)$$

$$= \ln(N_A^{-2/5}N_B^{1/2}\gamma^{-1/10}K_B^{1/10}) = \ln(N_A^{-2/5}N_B^{1/2}), \quad (47)$$

where the last equality is an approximation arrived at by comparing the relative magnitude of the different variables in the expression for K_B. The condition $\Delta G_A \ll \Delta G_B$, $D/R \gg 1$ is reached when

$$N_A \ll N_B^{5/4}\gamma^{-1/4}K_B^{1/4}. \quad (48)$$

The scaling relations (41), (42), (45), and (46) are identical to the results presented by Zhulina and Birshtein[9] for micelle formation in theta solvents.

C. Solubilization—unswollen core and swollen shell

The free energy of the micelle per block copolymer molecule in this case is given by the expression

$$\Delta G = g^{1/2}K_A + g^{1/2}K_B + \gamma N_A^{2/3}g^{-1/3}\phi_A^{-2/3} + K_L, \quad (49)$$

where ϕ_A for an unswollen core depends on g through Eq. (18). The analytical minimization of ΔG can be carried out by retaining all the terms, in contrast to the situation encountered earlier with Eq. (32). From the minimization of ΔG with respect to g, we can get the equilibrium aggregation number. This, when combined with Eq. (18), provides the scaling relations for R and ϕ_A,

$$g = N_A\gamma(K_A+K_B)^{-1},$$

$$R = N_A^{3/4}\gamma^{1/4}(K_A+K_B)^{-1/4}, \quad (50)$$

$$\phi_A = N_A^{-1/4}\gamma^{1/4}(K_A+K_B)^{-1/4}.$$

We can now consider the two limiting situations of small D/R and large D/R. In the limit of $D/R \ll 1$, the shell thickness D is obtained from Eqs. (27) and (50)

$$D = N_A^{-1/6}N_B\gamma^{1/6}\omega_B^{1/3}(K_A+K_B)^{-1/6}. \quad (51)$$

The parameters K_A and K_B are given by the expressions

$$K_A = 1 + \ln\left(\frac{R}{g^{1/2}}\right) = 1 + \ln[N_A^{1/4}\gamma^{-1/4}(K_A+K_B)^{1/4}]$$

$$= 1 + \ln(N_A^{1/4}), \quad (52)$$

$$K_B = \ln\left(1+\frac{D}{R}\right) = \frac{D}{R}$$

$$= N_A^{-11/12} N_B \gamma^{-1/12} \omega_B^{1/3} (K_A+K_B)^{1/12} = \frac{N_B}{N_A}. \quad (53)$$

The last equalities in the above two expressions are approximations, obtained as mentioned earlier.

In the opposite limit of $D/R \gg 1$, the shell thickness is estimated from Eqs. (27) and (50)

$$D = N_A^{1/5} N_B^{3/5} \gamma^{1/5} \omega_B^{1/5} (K_A+K_B)^{-1/5}. \quad (54)$$

The parameter K_A remains unaltered from that given by Eq. (52) since the expressions for g and R are the same in the two limits of D/R considered here. The parameter K_B is modified from that in Eq. (53) and is given by

$$K_B = \ln\left(1+\frac{D}{R}\right)$$
$$= \ln\left(\frac{D}{R}\right) = \ln[N_A^{-11/20} N_B^{3/5} \gamma^{-1/20} \omega_B^{1/5} (K_A+K_B)^{1/20}]$$
$$= \ln\left(\frac{N_B}{N_A}\right)^{3/5}, \quad (55)$$

where, as before, the last equality is an approximation.

D. Solubilization—unswollen core and unswollen shell

The free energy per molecule of the micelle ΔG is given by Eq. (49), while the overall volume fraction of the A segments in the micellar core ϕ_A is given by Eq. (18) as for Sec. IV C. Consequently, the scaling relations for g, R, and ϕ_A are identical to those for Sec. IV C. Thus,

$$g = N_A \gamma (K_A+K_B)^{-1},$$
$$R = N_A^{3/4} \gamma^{1/4} (K_A+K_B)^{-1/4}, \quad (56)$$
$$\phi_A = N_A^{-1/4} \gamma^{1/4} (K_A+K_B)^{-1/4}.$$

The shell thickness D can be estimated for the two limits of D/R being small or large, respectively. When $D/R \ll 1$, D is obtained from Eqs. (24) and (56)

$$D = N_A^{-1/4} N_B \gamma^{1/4} (K_A+K_B)^{-1/4}. \quad (57)$$

Correspondingly, the parameters K_A and K_B can be evaluated by introducing the expressions for g, R, and D in the definitions for these two parameters

$$K_A = 1+\ln\left(\frac{R}{g^{1/2}}\right)$$
$$= 1+\ln[N_A^{1/4} \gamma^{-1/4} (K_A+K_B)^{1/4}] = 1+\ln(N_A^{1/4}), \quad (58)$$

$$K_B = \ln\left(1+\frac{D}{R}\right) = \frac{D}{R} = \frac{N_B}{N_A}. \quad (59)$$

In the opposite limit of $D/R \gg 1$, the shell thickness is obtained from Eqs. (24) and (56)

$$D = N_A^{1/4} N_B^{1/2} \gamma^{1/4} (K_A+K_B)^{-1/4}. \quad (60)$$

The parameter K_A is unaltered from Eq. (58) since the expressions for R and g are not modified for the two limits of D/R. The parameter K_B is altered and is estimated from

$$K_B = \ln\left(1+\frac{D}{R}\right) = \ln\left(\frac{D}{R}\right) = \ln\left(\frac{N_B}{N_A}\right)^{1/2}. \quad (61)$$

E. Solubilization—swollen core and swollen shell

The free energy of the micelle per block copolymer molecule is given by Eq. (49) as for the previous two cases, but the volume fraction ϕ_A is now specified by Eq. (21). From the minimization of the free energy ΔG with respect to g, we obtain the equilibrium aggregation number

$$g = N_A^{12/11} \gamma^{10/11} \omega_A^{4/11} (K_A+K_B)^{-10/11}. \quad (62)$$

Introducing the above expression for g in Eq. (21), we get

$$R = N_A^{9/11} \gamma^{2/11} \omega_A^{3/11} (K_A+K_B)^{-2/11},$$
$$\phi_A = N_A^{-4/11} \gamma^{4/11} \omega_A^{-5/11} (K_A+K_B)^{-4/11}. \quad (63)$$

The shell thickness D and the parameters K_A and K_B can be determined for the two limiting values of small and large D/R, respectively. When $D/R \ll 1$, the shell thickness D can be calculated by combining Eqs. (27), (62), and (63). One obtains

$$D = N_A^{-2/11} N_B \gamma^{2/11} \omega_A^{-2/33} \omega_B^{1/3} (K_A+K_B)^{-2/11}. \quad (64)$$

The parameter K_A can be calculated based on the results obtained for g and R.

$$K_A = 1+\ln\left(\frac{R}{g^{1/2}}\right)$$
$$= 1+\ln[N_A^{3/11} \gamma^{-3/11} \omega_A^{1/11} (K_A+K_B)^{3/11}]$$
$$= 1+\ln(N_A^{3/11}). \quad (65)$$

In the above equation, the final approximation is made on the basis of an evaluation of the relative magnitude of all the variables appearing within the logarithmic factor as before. The parameter K_B can be calculated knowing D and R,

TABLE I. Scaling relations for micellization in good and theta solvents.

Variable	Uniform density core swollen shell (good S)	Uniform density core unswollen shell (theta S)
$\frac{D}{R} \ll 1$		
g	$N_A \gamma$	$N_A \gamma$
R	$N_A^{2/3} \gamma^{1/3}$	$N_A^{2/3} \gamma^{1/3}$
D	$N_A^{-1/9} N_B \gamma^{1/9} \omega_B^{1/3}$	$N_A^{-1/6} N_B \gamma^{1/6}$
K_B	$N_A^{-7/9} N_B \gamma^{-2/9} \omega_B^{1/3}$	$N_A^{-5/6} N_B \gamma^{-1/6}$
$\frac{D}{R} \gg 1$		
g	$N_A^{4/5} \gamma^{6/5} K_B^{-6/5}$	$N_A^{4/5} \gamma^{6/5} K_B^{-6/5}$
R	$N_A^{3/5} \gamma^{2/5} K_B^{-2/5}$	$N_A^{3/5} \gamma^{2/5} K_B^{-2/5}$
D	$N_A^{4/25} N_B^{3/5} \gamma^{6/25} \omega_B^{1/5} K_B^{-6/25}$	$N_A^{1/5} N_B^{1/2} \gamma^{3/10} K_B^{-3/10}$
K_B	$\ln(N_A^{-11/25} N_B^{3/5})$	$\ln(N_A^{-2/5} N_B^{1/2})$

TABLE II. Scaling relations for solubilization of a theta solubilizate.

Variable	Unswollen core (theta J) Swollen shell (good S)	Unswollen core (theta J) Unswollen shell (theta S)
g	$N_A \gamma (K_A + K_B)^{-1}$	$N_A \gamma (K_A + K_B)^{-1}$
R	$N_A^{3/4} \gamma^{1/4} (K_A + K_B)^{-1/4}$	$N_A^{3/4} \gamma^{1/4} (K_A + K_B)^{-1/4}$
ϕ_A	$N_A^{-1/4} \gamma^{1/4} (K_A + K_B)^{-1/4}$	$N_A^{-1/4} \gamma^{1/4} (K_A + K_B)^{-1/4}$
K_A	$1 + \ln(N_A^{1/4})$	$1 + \ln(N_A^{1/4})$
$\dfrac{D}{R} \ll 1$		
D	$N_A^{-1/6} N_B \gamma^{1/6} \omega_B^{1/3} (K_A + K_B)^{-1/6}$	$N_A^{-1/4} N_B \gamma^{1/4} (K_A + K_B)^{-1/4}$
K_B	N_B/N_A	N_B/N_A
$\dfrac{D}{R} \gg 1$		
D	$N_A^{1/5} N_B^{3/5} \gamma^{1/5} \omega_B^{1/5} (K_A + K_B)^{-1/5}$	$N_A^{1/4} N_B^{1/2} \gamma^{1/4} (K_A + K_B)^{-1/4}$
K_B	$\ln(N_B/N_A)^{3/5}$	$\ln(N_B/N_A)^{1/2}$

$$K_B = \ln\left(1 + \frac{D}{R}\right) = \frac{D}{R} = N_A^{-1} N_B \omega_A^{-1/3} \omega_B^{1/3} = \frac{N_B}{N_A}, \quad (66)$$

where the last equality is an approximation as in earlier equations. In the alternate limit of $D/R \gg 1$, the shell thickness is obtained from Eq. (27) after substituting for g from Eq. (62)

$$D = N_A^{12/55} N_B^{3/5} \gamma^{2/11} \omega_A^{4/55} \omega_B^{1/5} (K_A + K_B)^{-2/11}. \quad (67)$$

The parameter K_A is unaltered from that given by Eq. (65). The parameter K_B is estimated, with the usual approximation based on the relative magnitude of the different variables, to be

$$K_B = \ln\left(1 + \frac{D}{R}\right) = \ln\left(\frac{D}{R}\right)$$

$$= \ln(N_A^{-3/5} N_B^{3/5} \omega_A^{-1/5} \omega_B^{1/5}) = \ln\left(\frac{N_B}{N_A}\right)^{3/5} \quad (68)$$

F. Solubilization—swollen core and unswollen shell

The expression for the free energy ΔG is given by Eq. (49), while the volume fraction of A segments within the core ϕ_A is specified by Eq. (21) as for Sec. IV E. Thus, the scaling relations for g, R, and ϕ_A are unaltered compared to Sec. IV E. Therefore,

$$g = N_A^{12/11} \gamma^{10/11} \omega_A^{4/11} (K_A + K_B)^{-10/11},$$

$$R = N_A^{9/11} \gamma^{2/11} \omega_A^{3/11} (K_A + K_B)^{-2/11}, \quad (69)$$

$$\phi_A = N_A^{-4/11} \gamma^{4/11} \omega_A^{-5/11} (K_A + K_B)^{-4/11}.$$

The shell thickness D and the parameters K_A and K_B can be estimated for the two limiting cases of $D/R \ll 1$ and $D/R \gg 1$. For $D/R \ll 1$, the shell thickness D is obtained by introducing in Eq. (24) the equations for g and R from above. One obtains

$$D = N_A^{-3/11} N_B \gamma^{3/11} \omega_A^{-1/11} (K_A + K_B)^{-3/11}. \quad (70)$$

The parameter K_A can be estimated with the usual approximations as before

$$K_A = 1 + \ln\left(\frac{R}{g^{1/2}}\right)$$

$$= 1 + \ln[N_A^{3/11} \gamma^{-3/11} \omega_A^{1/11} (K_A + K_B)^{3/11}]$$

$$= 1 + \ln(N_A^{3/11}). \quad (71)$$

Similarly, the parameter K_B is also calculated approximately to be

$$K_B = \ln\left(1 + \frac{D}{R}\right) = \frac{D}{R}$$

$$= N_A^{-12/11} N_B \gamma^{1/11} \omega_A^{-4/11} (K_A + K_B)^{-1/11} = \frac{N_B}{N_A}. \quad (72)$$

In the opposite limit of $D/R \gg 1$, the shell thickness D is obtained from Eqs. (24) and (69)

$$D = N_A^{3/11} N_B^{1/2} \gamma^{5/22} \omega_A^{1/11} (K_A + K_B)^{-5/22}. \quad (73)$$

The parameter K_A is given by Eq. (71) since the expressions for R and g are not altered from the case of $D/R \ll 1$. The parameter K_B is calculated from

TABLE III. Scaling relations for solubilization of a good solubilizate.

Variable	Swollen core (good J) Swollen shell (good S)	Swollen core (good J) Unswollen shell (theta S)
g	$N_A^{12/11} \gamma^{10/11} \omega_A^{4/11} (K_A + K_B)^{-10/11}$	$N_A^{12/11} \gamma^{10/11} \omega_A^{4/11} (K_A + K_B)^{-10/11}$
R	$N_A^{9/11} \gamma^{2/11} \omega_A^{3/11} (K_A + K_B)^{-2/11}$	$N_A^{9/11} \gamma^{2/11} \omega_A^{3/11} (K_A + K_B)^{-2/11}$
ϕ_A	$N_A^{-4/11} \gamma^{4/11} \omega_A^{-5/11} (K_A + K_B)^{-4/11}$	$N_A^{-4/11} \gamma^{4/11} \omega_A^{-5/11} (K_A + K_B)^{-4/11}$
K_A	$1 + \ln(N_A^{3/11})$	$1 + \ln(N_A^{3/11})$
$\dfrac{D}{R} \ll 1$		
D	$N_A^{-2/11} N_B \gamma^{2/11} \omega_A^{-2/33} \omega_B^{1/3} (K_A + K_B)^{-2/11}$	$N_A^{-3/11} N_B \gamma^{3/11} \omega_A^{-1/11} (K_A + K_B)^{-3/11}$
K_B	N_B/N_A	N_B/N_A
$\dfrac{D}{R} \gg 1$		
D	$N_A^{12/55} N_B^{3/5} \gamma^{2/11} \omega_A^{4/55} \omega_B^{1/5} (K_A + K_B)^{-2/11}$	$N_A^{3/11} N_B^{1/2} \gamma^{5/22} \omega_A^{1/11} (K_A + K_B)^{-5/22}$
K_B	$\ln(N_B/N_A)^{3/5}$	$\ln(N_B/N_A)^{1/2}$

$$K_B = \ln\left(1 + \frac{D}{R}\right)$$

$$= \ln\left(\frac{D}{R}\right)$$

$$= \ln[N_A^{-6/11} N_B^{1/2} \gamma^{1/22} \omega_A^{-2/11} (K_A + K_B)^{-1/22}]$$

$$= \ln\left(\frac{N_B}{N_A}\right)^{1/2}. \tag{74}$$

V. CONCLUSIONS

A theory of solubilization of low molecular weight compounds in spherical block copolymer micelles is developed here, employing a scaling approach and utilizing the analogy between block copolymer micelles and star polymers. The theory thus allows for the existence of a radial concentration variation within the core and the shell regions of the micelle, in contrast to our earlier mean-field theory where concentration homogeneity in the two regions was assumed. Employing the results derived by Daoud and Cotton for the conformation of a star polymer, we relate the core radius R, the shell thickness D, and the volume fraction of the A segments within the core ϕ_A as well as the free energy of micelle formation ΔG to the aggregation number g of the micelle. From the minimization of the micelle free energy, scaling relations are derived for all the structural parameters of the micelle. Various situations of interest are considered including when the solvent S is a good or theta solvent for the shell block B, and when the solubilizate J is a good or theta solvent for the core block A. The results obtained in this study are summarized for convenient reference in Table I for micellization in theta and good solvents, in Table II for solubilization of theta solubilizates, and in Table III for solubilization of good solubilizates. Expressions for the shell thickness D when D/R is close to unity are not given since D will be comparable to R under these conditions and the scaling relations for R are provided in the tables. Experimental data are not available at present to compare against the predicted scaling relations, and such measurements are being undertaken in our laboratory.

APPENDIX

D thickness of the micellar shell;

g aggregation number of the micelle;

k Boltzmann's constant;

N_A effective number of repeat units in block A of the copolymer;

N_B effective number of repeat units in block B of the copolymer;

$n(r)$ number of segments within a blob located at r;

R radius of the core of the micelle;

R_p radius of the solubilizate pool in the micelle core;

r radial distance from the center of the star polymer or of the micelle;

T temperature of the system;

$\alpha(r)$ chain expansion parameter for a blob located at r;

γ interfacial tension between the micellar core and the micellar shell;

γ_{AS} interfacial tension between the A block and solvent S;

γ_{JS} interfacial tension between solubilizate J and solvent S;

γ_{AB} interfacial tension between the A block and B block;

γ_{BJ} interfacial tension between solubilizate J and the B block;

ΔG free energy per molecule of an isolated block copolymer micelle;

η overall volume fraction of solubilizate J in the micellar core;

$\xi(r)$ the size of a blob located at r;

τ thickness of the interfacial region surrounding the core;

$\phi(r)$ local concentration of polymer segments within a blob located at r;

ϕ_A overall volume fraction of the A block in the micellar core;

χ_{BS} Flory interaction parameter between the B block and solvent S;

χ_{AJ} Flory interaction parameter between the A block and solubilizate J;

ω excluded volume parameter of a polymer in a solvent;

ω_A excluded volume parameter of the A block in solubilizate J;

ω_B excluded volume parameter of the B block in solvent S.

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