Comparison of Solubilization of Hydrocarbons in (PEO–PPO) Diblock versus (PEO–PPO–PEO) Triblock Copolymer Micelles

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The solubilization of hydrocarbons by micelles formed of diblock and symmetric triblock copolymers in water are compared in the framework of a mean-field theory of solubilization. The block copolymers contain poly(ethylene oxide) as the hydrophilic block and poly(propylene oxide) as the hydrophobic block and are designated as $E_X P_Y E_X$ or $E_W P_Z$ (where E and P denote ethylene and propylene oxides and the subscripts denote the number of segments). In the presence of a variety of aromatic and aliphatic hydrocarbon solubilizates, the core radius, corona thickness, and aggregation number of the micelle and also the volume fraction of the hydrocarbon solubilized in the core are predicted. The calculations show that for identical molecular weights and block compositions, the diblock ($E_{200} P_{64}$) copolymer micelles have a much larger core radius, corona thickness, aggregation number, and volume fraction of the hydrocarbon solubilized in the core compared with the symmetric triblock ($E_{100} P_{64} E_{100}$) copolymer micelles. In contrast, the diblock copolymer ($E_{100} P_{32}$), having the same block composition but half the molecular weight of the symmetric triblock copolymer ($E_{100} P_{64} E_{100}$), gives rise to micelles having the same core radius, corona thickness, and volume fraction of the hydrocarbon solubilized as the micelles formed of the triblock copolymer, and an aggregation number twice that of the triblock copolymer micelle. © 1996 Academic Press, Inc.

Key Words: block copolymer micelles; solubilization in micelles; PEO–PPO diblock copolymers; PEO–PPO–PEO triblock copolymers; solubilization of hydrocarbons; thermodynamics of solubilization.

1. INTRODUCTION

Block copolymer molecules consisting of hydrophobic and hydrophilic blocks aggregate in aqueous solutions, forming multimolecular micelles. In these micelles, the hydrophobic blocks constitute the core and the hydrophilic blocks along with the solvent water form the corona. One of the most useful properties of micelles is their ability to enhance the aqueous solubility of hydrophobic substances. This phenomenon, referred to as solubilization, is made possible by the incorporation of the solubilizates in the hydrophobic microenvironment offered by the micellar core (1–3). Because of the solubilization power of micelles, aqueous block copolymer solutions hold great promise as substituents for organic solvents in many industrial applications.

In an earlier paper (4), we presented experimental results on the solubilization of aliphatic and aromatic hydrocarbons in micelles formed of poly(ethylene oxide)–poly(propylene oxide)(PEO–PPO) and poly(vinyl pyrrolidone)–polystyrene (PVP–PS) block copolymers. Further, the selectivity in the solubilization behavior was explored via measurements of the solubilization capacities of benzene and hexane when their binary mixtures were solubilized. Interesting results displaying large solubilization capacities and high selectivity for aromatics over aliphatics were obtained in block copolymer micelles compared with conventional low-molecular-weight surfactant micelles. Subsequently, we developed a theory of solubilization in block copolymer micelles using a mean-field approach (5) and compared the theoretical predictions for the PEO–PPO diblock copolymer micelle with experimental solubilization data.

In the context of the above-mentioned experimental (4) and theoretical (5) studies, this paper has two principal goals. The first goal is linked to the fact that many commercially available block copolymers made of PEO and PPO blocks are symmetric triblock copolymers. Therefore, it is of interest to predict the solubilization behavior in a triblock copolymer micelle and compare it against the predictions for a diblock copolymer micelle. The second goal stems from the need to improve our earlier theory of solubilization (5) which assumed uniform segment densities in the core and the corona regions of the micelle while at the same time treating the chains to be stretched uniformly along their length (uniform concentration–uniform deformation model). However, to maintain uniform concentrations in the core and the corona, it is necessary for the chains to be stretched nonuni-

TABLE 1

Molecular Properties of the Hydrocarbon Solubilizates and Solubilization Capacity of Block Copolymer Micelles for Hydrocarbons at 25°C

| Solubilizate | Molecular properties of solubilizates | | | |
	v_J (Å^3)	σ_{JW} (dyn/cm)	δ_J (MPa$^{1/2}$)	mmol solubilized/g of PPO block[a]
Benzene	146	33.93	18.80	11.67
Toluene	176	36.1	18.19	6.33
o-Xylene	200	36.1	18.40	4.0
Ethyl benzene	204	38.4	17.99	5.67
Cyclohexane	179	50.2	16.76	1.97
Hexane	217	50.7	14.92	0.667
Heptane	243	51.2	15.13	0.567
Octane	270	51.5	15.53	0.5
Decane	323	52	15.74	0.387

[a] Experimental results obtained in our earlier study (4) using block copolymer of molecular weight 12,500, with 70 wt% PEO and 30 wt% PPO.

formly, as clearly enunciated by Semenov (6). Hence, the second goal of this paper is to formulate the uniform concentration–nonuniform deformation model to predict the solubilization behavior of hydrocarbons in block copolymer micelles. Micellar models based on such nonuniform chain stretching have been developed by us for conventional surfactants (7).

Alternate micellar models allowing for concentration inhomogeneities in the corona region (7) or in both the core and the corona regions (8) have also been formulated in our earlier studies. The former model is based on a mean-field description, whereas the latter theory is based on a scaling approach exploiting the analogy between spherical micelles and star polymers. Another approach is that of Hurter *et al.* (9) involving self-consistent field calculations, which allow the prediction of composition profiles in the core and the corona regions of the micelle.

2. SUMMARY OF EXPERIMENTAL RESULTS

The solubilization capacities of block copolymer micelles for aromatic and aliphatic hydrocarbons reported in Ref. (4) were determined using the gas chromatographic method. The block copolymer molecule employed was composed of PEO and PPO blocks with a total molecular weight of 12,500 and having 30% PPO (Polysciences Inc.). This corresponds to a polymer having approximately 200 ethylene oxide and 64 propylene oxide segments. The limiting amounts of solubilization of a number of aromatic and aliphatic hydrocarbons in aqueous solutions of 10 wt% block copolymer are listed in Table 1, expressed as millimoles solubilized per gram of the hydrophobic PPO block of the copolymer. Any excess hydrocarbon

added to the system will form a separate hydrocarbon phase coexisting with the aqueous copolymer solution.

Also listed in Table 1 are some important molecular characteristics of the solubilizates: molecular volume (v_J), interfacial tension against water (σ_{JW}), and Hildebrand–Scatchard solubility parameter (δ_J) values. The subscript J denotes the solubilizate, W refers to water, and A and B denote the hydrophobic and the hydrophilic blocks of the copolymer, respectively. The Flory interaction parameter χ_{AJ} accounts for the interactions between the core forming block A of the copolymer and the solubilizate J. This parameter is estimated (4) from knowledge of the Hildebrand solubility parameters of both A and J via the relation $\chi_{AJ} = (\delta_A - \delta_J)^2 v_J / kT$, where δ_A is the solubility parameter for the A block, k is the Boltzmann constant, and T is the absolute temperature. Taking $\delta_A = 19$ MPa$^{1/2}$ for PPO (4) and using the molecular properties of solubilizates listed in Table 1, one can calculate χ_{AJ} for all the solubilizates.

The experimental solubilization data obtained in Ref. (4) are empirically correlated via the relation

$$\mathrm{MSR} = a\chi_{AJ}^{-b} = a\left[\frac{(\delta_A - \delta_J)^2 v_J}{kT}\right]^{-b} \qquad [1]$$

for both block copolymers investigated. Here, MSR is the ratio of the moles of hydrocarbon solubilized to the moles of block copolymer in solution, and a and b are positive constants dependent on the block copolymer molecule. In a recent study, such a correlation has been found to describe well the experimental solubilization data for aliphatic, aromatic, cyclic, and chlorinated hydrocarbons and esters in poly(styrene)–poly(methacrylic acid) block copolymer micelles (10). This empirical correlation suggests that solubilizate J–core block A compatibility ($\delta_A - \delta_J$ is small), as well as a smaller molecular volume of the solubilizate v_J, lead to significantly large amounts solubilized.

In contrast to an empirical correlation, a theory of solubilization can a priori predict the volume fraction of the solubilizate inside the micellar core region as a function of the molecular properties of the copolymer, the solvent, and the solubilizate. In addition, a theory can predict all the microstructural features of the micelle as well, such as the core radius, the thickness of the corona, and the aggregation number. Such a theory, applicable to both diblock and symmetric triblock copolymer molecules, is outlined below. Predictions of various microstructural features of micelles containing solubilizates are given in this paper, although no experimental data are currently available for comparison. Recent studies have begun to address this need; for example, the hydrodynamic radii of micelles containing solubilizates determined by light scattering are given for another block copolymer system in Ref. (10). We note, however, that its

decomposition into core radius and corona thickness is not possible in the absence of additional information on the aggregation number of the micelles.

3. THERMODYNAMIC THEORY OF SOLUBILIZATION

Size and Composition Distribution of Micelles

The micelles present in solution may contain varying numbers of copolymer and solubilizate molecules. The size and composition distribution of micelles at equilibrium is obtained by minimizing the total free energy of the system. The system includes solvent molecules, singly dispersed copolymer, and solubilizate molecules and micelles of various sizes and compositions. Each of the species in the solution, including micelles of different sizes and compositions, is treated as a distinct chemical component. The standard state of the solvent is defined as the pure solvent, whereas the standard states of all the other components are taken as those at infinitely dilute solution conditions. The standard chemical potentials of the solvent water (W), the singly dispersed copolymer, the singly dispersed solubilizate (J), and micelles of aggregation number g containing j solubilizate molecules are denoted by μ_W^0, μ_1^0, μ_{1J}^0, and μ_g^0, respectively. Denoting the mole fraction of species i by X_i, the micelle size and composition distribution equation can be written (7, 8) in the form

$$X_g = X_1^g X_{1J}^j \exp - \left(\frac{\mu_g^0 - g\mu_1^0 - j\mu_{1J}^0}{kT} \right). \qquad [2]$$

In writing Eq. [2], it is assumed either that intermicelle interactions are not present or that they do not affect the size distribution. Also, the system entropy of the multicomponent solution is written as for an ideal solution. In dilute solutions such as those of interest here, the intermicellar interactions are not important. Therefore, one may neglect the free energy contributions associated with such interactions. The consequences of using a few plausible models of system entropy in the theory of micellization have been analyzed in detail in Ref. (11). It was found that for nonionic systems such as those considered here, the choice of a model for the system entropy has no influence on the micellar structural parameters, but affects only the magnitude of the critical micelle concentration (CMC). Further, the CMC predicted assuming one entropy model can be related via a simple scale factor to the CMC that would result from another entropy model (11).

If one wants to calculate the limiting (or maximum) amount of solubilization of a compound that is possible inside the micelle, then the concentration of the singly dispersed solubilizate X_{1J} in water should be its saturation concentration X_{1J}^*. This condition is defined by the equilibrium relation

$$\mu_J^H = \mu_{1J}^0 + kT \ln X_{1J}^*. \qquad [3]$$

Since an excess solubilizate phase comes into existence when the aqueous solution is saturated with the solubilizate, the standard state μ_J^H of the solubilizate refers to a pure solubilizate phase. Denoting by f the fractional saturation of water with the solubilizate (i.e., X_{1J}/X_{1J}^*), the micelle size and composition distribution equation becomes

$$X_g = X_1^g f^{j/g} \exp - \left(\frac{g\Delta\mu_g^0}{kT} \right),$$

where

$$\Delta\mu_g^0 = \left(\frac{\mu_g^0}{g} - \mu_1^0 - \frac{j}{g}\mu_{1J}^H \right). \qquad [4]$$

The factor $\Delta\mu_g^0$ represents the change in the standard-state free energy when a singly dispersed block copolymer molecule in water and j/g solubilizate molecules in their pure phase are transferred to an isolated micelle in water. The solubilization limit is achieved for $f = 1$, when the aqueous micellar phase coexists with the pure solubilizate phase. All predictions given in this paper are for this condition since the experimental data in Ref. (4) were obtained corresponding to the solubilization limit. Our calculations have shown that the size and composition distribution of micelles is very narrow and it is reasonable to assume that the micelles are all of a single size and composition (5).

Pseudophase Description of Micelles

To simplify numerical computational efforts, the micelle containing the solubilizates can be represented as a pseudophase in equilibrium with the singly dispersed solubilizate and copolymer molecules in solution. For aggregates exhibiting narrow size distribution, this representation provides results practically identical to those obtained from the detailed size distribution calculations. The equilibrium characteristics of the micelle in the pseudophase approximation are obtainable from the condition

$$\frac{\partial}{\partial g}\left[\frac{\Delta\mu_g^0}{kT} \right] = 0, \quad \frac{\partial}{\partial j}\left[\frac{\Delta\mu_g^0}{kT} \right] = 0$$

$$\text{at } g = g_{opt}, j = j_{opt} \quad [5]$$

where g_{opt} and j_{opt} refer to the numbers of block copolymer and solubilizate molecules, respectively, constituting the optimal or equilibrium aggregate. The CMC in the pseudophase approximation is calculated from

$$X_{CMC} = \exp\left[\frac{\Delta\mu_g^0}{kT}\right] \quad \text{at } g = g_{opt}, j = j_{opt}. \qquad [6]$$

The magnitude of $\Delta\mu_g^0$ controls the CMC as shown by Eq. [6]. In contrast, the equilibrium structural features of the micelle are determined by how this standard free energy difference depends on the variables g and j, as is evident from Eq. [5]. To formulate an expression for this free energy difference, the geometrical features of the micelle should be specified.

Geometrical Properties of Aggregates

Two structural descriptions of spherical aggregates can be visualized depending on how the solubilizate is contained inside the block copolymer micelle (Fig. 1). These descriptions result by analogy with the structural models employed for simple solubilization and microemulsification, respectively, in systems involving low-molecular-weight surfactants. The type a structure is analogous to that used for simple solubilization. Here, the micellar core is made up of the solvent incompatible A blocks and the solubilizate J. The solvent compatible B blocks and solvent W are present in the corona region of the micelle. The type b structure is analogous to that used for droplet microemulsions, with the core region separated into two parts. Pure solubilizate J is allowed to exist in the inner core of the micelle. This solubilizate domain is surrounded by the outer core region consisting of the A block and the solubilizate J. The corona of the micelle contains the B block and the solvent W as in the type a structure. In the absence of a pool of pure solubilizate J in the inner core, the type b structure reduces identically to type a. Free energy calculations of the kind described below showed that for the systems considered in this paper, the condition of minimum free energy always occurred corresponding to a zero size for the pure solubilizate pool. Thus, the thermodynamic equilibrium criterion always favored the occurrence of the type a structure. Consequently, free energy expressions corresponding to only the type a structure are discussed here.

We note that nonspherical aggregate structures are not considered in this paper. Such structures (cylinders, vesicles, or lamellae, for example) can come into existence depending on the composition and molecular weight of the block copolymer. The formation of nonspherical aggregates has been modeled in our recent study (12) from which we predict that for the molecules examined in this paper, only spherical micelles result in aqueous solutions.
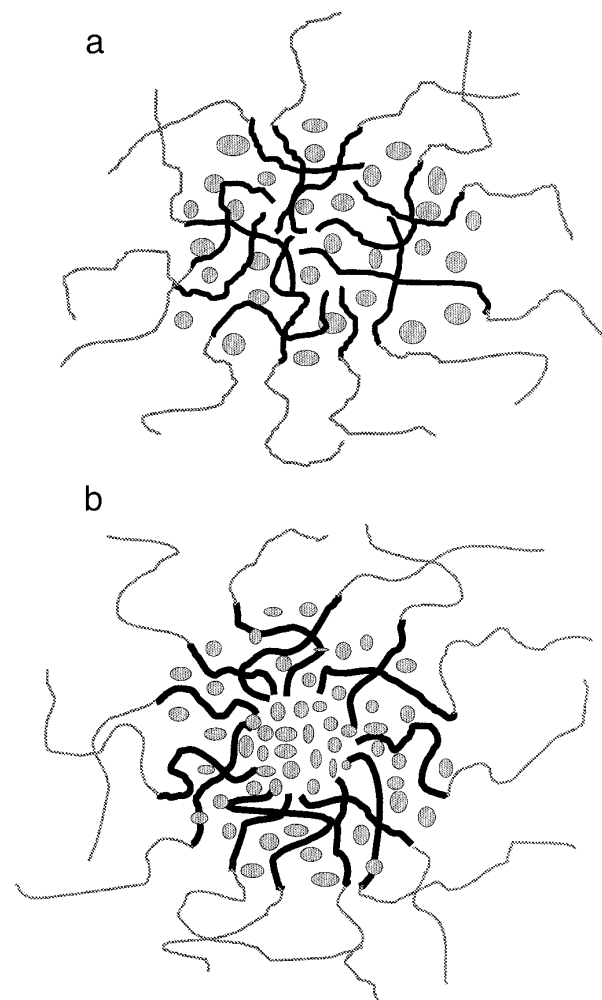

FIG. 1. Schematic representation of a spherical block copolymer micelle containing the solubilizate. The darker lines denote the hydrophobic block, and the lighter lines, the hydrophilic block. In the type a structure, all of the solubilizate molecules interact with the core block. In the type b structure, a part of the solubilizate molecules are present in a separate domain while the remaining interact with the core block.

We denote the molecular volumes of the A and the B segments, the solubilizate, and the solvent by v_A, v_B, v_J, and v_W, respectively. The characteristic lengths of the A and the B segments are denoted by L_A ($=v_A^{1/3}$) and L_B ($=v_B^{1/3}$). The variables N_A and N_B refer to the number of segments of block A and block B for the AB diblock as well as the BAB triblock copolymers, implying that the BAB triblock copolymer has two terminal blocks of size $N_B/2$ attached to a middle block of size N_A. We use the variable R to denote the hydrophobic core radius, D for the corona thickness, and a for the surface area of the aggregate core per constituent block copolymer molecule. The micelle core volume V_C is calculated as the sum of the volumes of the A blocks and the solubilizate molecules, $V_C = gN_Av_A + jv_J$. The volume

TABLE 2
Geometrical Properties of Spherical Aggregates

Property	Geometrical relation
Core volume (V_C)	$4\pi R^3/3$
Corona volume (V_S)	$V_C [(1 + D/R)^3-1]$
Aggregation number of micelles (g)	$V_C \phi_A/(N_A v_A)$
Area per molecule of core surface (a)	$3N_A v_A/(R\phi_A)$
Volume fraction of B in corona (ϕ_B)	$(N_B v_B)/(N_A v_A) \phi_A (V_C/V_S)$
Volume fraction of solubilizate in core (η)	$1-\phi_A$

of the corona region is denoted by V_S. The volume fraction of the solubilizate molecules in the core is denoted by η ($= j v_J/(g N_A v_A + j v_J)$). The concentrations of segments are assumed to be uniform in the core as well as in the corona, with ϕ_A standing for the volume fraction of the A segments in the core ($\phi_A = 1 - \eta$), and ϕ_B for the volume fraction of the B segments in the corona. The shape of the micelle and the assumption of incompressibility lead to the geometrical relations summarized in Table 2. If any three structural variables are specified all the remaining geometrical variables can be calculated through the relations given in Table 2. For convenience, R, D, and η (or ϕ_A) are chosen as the independent variables.

Model for the Free Energy of Solubilization

An expression for the free energy of solubilization $\Delta\mu_g^0$ defined in Eq. [4] is developed by considering all the physicochemical changes accompanying the transfer of the solubilizate molecule from its pure phase and the singly dispersed copolymer molecule from the infinitely dilute aqueous solution state to an isolated micelle also in the infinitely dilute solution state. First, the transfer of the solubilizate and the singly dispersed copolymer to the micellar core is associated with changes in the state of dilution and in the state of deformation of the A block, including the swelling of the A blocks inside the core by the solubilizate J. Second, the B block of the singly dispersed copolymer is transferred to the corona region of the micelle, and this transfer process also involves changes in the states of dilution and deformation of the B block. Third, the formation of the micelle localizes the copolymer such that the A block is confined to the core while the B block is confined to the corona. Fourth, the formation of the micelle is associated with the generation of an interface between the micelle core made up of A blocks and solubilizate J and the micelle corona consisting of solvent W and B blocks. All these changes contribute to the free energy of solubilization in the case of the diblock and the triblock copolymers. Further, in the case of a BAB triblock copolymer, folding or loop formation of the A block occurs, ensuring that the B blocks at the two ends are in the aqueous domain while the folded A block is within the hydrophobic

core of the micelle. This provides an additional free energy contribution. The free energy of solubilization can be obtained as the sum of the above contributions:

$$(\Delta\mu_g^0) = (\Delta\mu_g^0)_{A,dil} + (\Delta\mu_g^0)_{A,def} + (\Delta\mu_g^0)_{B,dil} + (\Delta\mu_g^0)_{B,def}$$
$$+ (\Delta\mu_g^0)_{loc} + (\Delta\mu_g^0)_{int} + (\Delta\mu_g^0)_{loop}. \quad [7]$$

Expressions for each of these contributions are formulated below.

Change in State of Dilution of Block A

In the singly dispersed copolymer molecule, the A block is in a collapsed state, minimizing its interactions with the solvent. We consider the region consisting of the collapsed A block with some solvent entrapped in it to be a spherical globule, whose diameter $2R_{\infty A}$ is equal to the end-to-end distance of block A in the solvent. The volume of this spherical region is denoted by $V_{\infty A}$. The chain expansion parameter α_A describes the swelling of the polymer block A by the solvent W,

$$V_{\infty A} = \frac{4\pi R_{\infty A}^3}{3}, \ 2R_{\infty A} = \alpha_A N_A^{1/2} L_A,$$

$$\alpha_A = \left(\frac{6}{\pi}\right)^{1/3} N_A^{-1/6} \phi_{A1}^{-1/3}, \quad [8]$$

where ϕ_{A1} ($= N_A v_A/V_{\infty A}$) is the volume fraction of A segments within the monomolecular globule. The first equality in Eq. [8] follows from geometry; the second equality is based on the definition of the chain expansion parameter α_A, taking ($N_A^{1/2} L_A$) as the unperturbed end-to-end distance of block A. The third equality is obtained by combining the first two in conjunction with the definition for ϕ_{A1}. The volume fraction ϕ_{A1} is calculated (5) from the condition of osmotic equilibrium between the monomolecular globule treated as a distinct phase and the solvent surrounding it, as suggested by de Gennes (13):

$$\ln(1 - \phi_{A1}) + \phi_{A1} + \chi_{AW}\phi_{A1}^2 = 0. \quad [9]$$

In Eq. [9], χ_{AW} is the Flory interaction parameter between the pure A polymer and water.

In the micelle, the A block is confined to the core region, where it is swollen by the solubilizate J. We consider this region to be uniform in concentration with a volume fraction ϕ_A of A segments and η ($=1 - \phi_A$) of the solubilizate. A mean-field description is employed for calculating the free energy of this region. The difference in the dilution of block A from its singly dispersed state to the micellized state makes a free energy contribution given by the relation

$$\frac{(\Delta\mu_g^0)_{A,dil}}{kT}$$

$$= N_A \left[\frac{v_A}{v_J} \frac{1 - \phi_A}{\phi_A} \ln(1 - \phi_A) + \frac{v_A}{v_J} (1 - \phi_A)\chi_{AJ} \right]$$

$$- N_A \left[\frac{v_A}{v_W} \frac{1 - \phi_{A1}}{\phi_{A1}} \ln(1 - \phi_{A1}) + \frac{v_A}{v_W} (1 - \phi_{A1})\chi_{AW} \right]$$

$$+ \left(\frac{\sigma_{AW}L_A^2}{kT} \right) \frac{6}{\alpha_A N_A^{1/2}} \right] \quad [10]$$

In this equation, the first two terms account for the entropic and enthalpic contributions arising from the mixing of pure A block and the pure solubilizate J within the micellar core. They are written in the form of the Flory expression for the swelling of a network (14) by a solvent. The third and the fourth terms account for the entropic and enthalpic changes associated with the removal of A block from its infinitely dilute state in water to a pure A state. These terms are written in the framework of the Flory expression (14) for an isolated polymer molecule. The last term accounts for the fact that the interface of the globule of the singly dispersed A block disappears on micellization. This term is written as the product of the interfacial tension (σ_{AW}) between pure A and solvent W, the surface area of the globule ($4\pi R_{\infty A}^2$), and the factor ϕ_{A1} (volume fraction of polymer A in the globule) to account for the reduction in the contact area between block A and solvent W caused by the presence of some water molecules inside the monomolecular globule. If the interfacial tension σ_{AW} is not available from direct measurements, it can be estimated using the relation $\sigma_{AW} = (\chi_{AW}/6)^{1/2}(kT/L^2)$, where $L = v_W^{1/3}$. Such a relation is usually employed for the calculation of polymer-polymer interfacial tensions.

Change in State of Deformation of Block A

In the singly dispersed state of the copolymer, the conformation of the A block is characterized by the chain expansion parameter α_A, which is the ratio between the actual end-to-end distance and the unperturbed end-to-end distance of the polymer block. The free energy of this deformation is written using the Flory expression (14) derived for an isolated polymer molecule. Within the micelle, the A block is stretched nonuniformly, with the chain ends occupying a distribution of positions within the core while ensuring that the core has a uniform concentration. The free energy contribution allowing for nonuniform chain deformation is calculated using the analysis of chain packing pioneered by Semenov (6). In the case of a BAB triblock copolymer, the A block deformation is calculated by considering the folded A block

of size N_A to be equivalent to two A blocks of size $N_A/2$. On this basis, one obtains

$$\frac{(\Delta\mu_g^0)_{A,def}}{kT} = \left[q \left(\frac{p\pi^2}{80} \right) \frac{R^2}{(N_A/q)L_A^2} \right]$$

$$- \left[\frac{3}{2} (\alpha_A^2 - 1) - \ln \alpha_A^3 \right], \quad [11]$$

where $q = 1$ for an AB diblock copolymer and $q = 2$ for a BAB triblock copolymer having a middle hydrophobic block. The parameter p is dependent on aggregate shape and has the value of 3 for spherical micelles (7). In Eq. [11], the first term represents the A-block deformation free energy in the micelle, whereas the second term corresponds to the deformation free energy in the singly dispersed copolymer.

Change in State of Dilution of Block B

In the singly dispersed state of the copolymer, the polymer block B is swollen with the solvent. As mentioned before, N_B denotes the size of the B block for the AB diblock copolymer, whereas for a symmetric BAB triblock copolymer, the end blocks are of equal size $N_B/2$. We consider this swollen B block to be a sphere, whose diameter $2R_{\infty B}$ is equal to the end-to-end distance of isolated block B in the solvent. The volume of this spherical region is denoted by $V_{\infty B}$, while ϕ_{B1} ($= N_B v_B/V_{\infty B}$) is the volume fraction of B segments within the monomolecular globule:

$$V_{\infty B} = \frac{4\pi R_{\infty B}^3}{3}, \quad 2R_{\infty B} = \alpha_B(N_B/q)^{1/2}L_B. \quad [12]$$

The second equality in Eq. [12] is based on the definition of the chain expansion parameter α_B, which can be estimated using the expression developed by Flory (14). In the Flory expression for α_B, Stockmayer (15) has suggested decreasing the numerical coefficient by approximately a factor of 2 to ensure consistency with the results obtained from perturbation theories of excluded volume. Consequently, one can estimate α_B as the solution of

$$\alpha_B^5 - \alpha_B^3 = 0.88(1/2 - \chi_{BW})(N_B/q)^{1/2} \quad [13]$$

where χ_{BW} is the Flory interaction parameter between the B block and water.

In the micelle, the B blocks are present in the corona region of volume V_S. This region is assumed to be uniform in concentration, with ϕ_B ($= gN_B v_B/V_S$) being the volume fraction of the B segments in the corona. The free energy of the corona region can be written using the Flory expression (14) for a network swollen by the solvent. Therefore,

the difference in the states of dilution of the B block on micellization provides the following free energy contribution:

$$
\begin{aligned}
\frac{(\Delta\mu_g^0)_{B,dil}}{kT} &= N_B\left[\frac{v_B}{v_W}\frac{1-\phi_B}{\phi_B}\ln(1-\phi_B) + \frac{v_B}{v_W}(1-\phi_B)\chi_{BW}\right] \\
&\quad - N_B\left[\frac{v_B}{v_W}\frac{1-\phi_{B1}}{\phi_{B1}}\ln(1-\phi_{B1})\right. \\
&\quad \left. + \frac{v_B}{v_W}(1-\phi_{B1})\chi_{BW}\right]. \quad [14]
\end{aligned}
$$

The first two terms in Eq. [14] describe the entropic and enthalpic contributions to the free energy of swelling of the B block by the solvent in the corona region of the micelle, whereas the last two terms refer to the corresponding contributions in the singly dispersed copolymer molecule.

Change in State of Deformation of Block B

In the singly dispersed state, the B block has a chain conformation characterized by the chain expansion parameter α_B. In the micelle, the B block is stretched nonuniformly over the micelle corona so as to ensure that the concentration in the corona region is uniform. Semenov (6) has shown that the estimate for the chain deformation energy, assuming that the termini of all B blocks lie at distance D from the core surface, is not very different form that calculated assuming a distribution of chain termini at various positions within the corona. On this basis, one can write (12)

$$
\begin{aligned}
\frac{(\Delta\mu_g^0)_{B,def}}{kT} &= \left[q\,\frac{3}{2}\,\frac{L_B R}{(a/q)\phi_B}\,P\right] \\
&\quad - q\left[\frac{3}{2}(\alpha_B^2 - 1) - \ln\alpha_B^3\right], \quad [15]
\end{aligned}
$$

where a is the surface area per molecule of the micelle core, $q = 1$ for AB diblock and $q = 2$ for BAB triblock, as before, and P is a shape-dependent function given by $P = (D/R)/[1 + (D/R)]$, for spheres (12). The first term in Eq. [15] represents the free energy of deformation of the B block in the micellar corona, whereas the second term denotes the corresponding free energy in the singly dispersed copolymer molecule.

Localization of the Copolymer Molecule

On micellization, the copolymer becomes localized in the sense that the joint linking blocks A and B in the copolymer is constrained to remain in the interfacial region rather than occupying all the positions available in the entire volume of the micelle. The entropic reduction associated with localization is modeled using the concept of configurational volume restriction. Thus, the localization free energy is calculated on the basis of the ratio between the volume available to the A–B joint in the interfacial shell of the micelle (surrounding the core and having a thickness L_B) and the total volume of the micelle:

$$
\frac{(\Delta\mu_g^0)_{loc}}{kT} = -q\,\ln\left[\frac{dL_B}{R(1 + D/R)^d}\right]. \quad [16]
$$

Here, d refers to the dimensionality of aggregate growth and is 3 for spherical micelles (12).

Formation of Micellar Core–Solvent Interface

When a micelle forms, an interface is generated between the core region consisting of the A block and the solubilizate J and the corona region consisting of the B block and the solvent W. The free energy of formation of this interface is estimated as the product of the surface area of the micellar core and an interfacial tension characteristic of this interface. The appropriate interfacial tension is that between a solution of block A and solubilizate J in the micelle core and a solution of block B and solvent W in the micellar corona. Since the corona region is often very dilute in block B, the interfacial tension can be approximated as that between the solvent W and a solution of the A block and the solubilizate J in the micelle core. Denoting the polymer A–solvent W interfacial tension by σ_{AW} and the solubilizate J–solvent W interfacial tension by σ_{JW}, the free energy of generation of the micellar core–solvent interface is calculated from

$$
\begin{aligned}
\frac{(\Delta\mu_g^0)_{int}}{kT} &= \frac{\sigma_{agg}}{kT}\,a, \\
\sigma_{agg} &= \sigma_{AW}\phi_A + \sigma_{JW}(1 - \phi_A). \quad [17]
\end{aligned}
$$

Here, the interfacial tension of a polymer solution of block A and solubilizate J against another liquid W is approximated to be the composition-averaged interfacial tensions of pure polymer A and pure solubilizate J against the solvent W. The volume fraction is used as the composition variable. Such a simple dependence of the interfacial tension on bulk solution composition is not generally obeyed in the case of free solutions of polymers or of low-molecular-weight components. The origin of the deviation from linearity lies

in the preferential adsorption or depletion of one of the components at the interface, which causes the surface composition to differ from the bulk composition (16); however, the micellar interface is different from the interface of a free polymer solution. Specifically, because of the localization of the A–B link at the interface, the segments of the A blocks are forced to be at the interface independent of any selective adsorption or depletion. This would diminish the difference between the surface and bulk compositions in the micellar core when compared with that in a free polymer solution. Consequently, the composition averaging of interfacial tension expressed by Eq. [17] is taken as a reasonable approximation in the present calculations. An alternate approach to estimating the interfacial tension by calculating the interface composition between two bulk solutions has been explored in our study of solubilization in low-molecular-weight surfactant micelles (8).

Backfolding or Looping in Triblock Copolymer

The backfolding or looping of the middle block in a BAB triblock copolymer contributes an entropic term to the free energy of solubilization. This contribution is absent for the case of a diblock copolymer. Jacobsen and Stockmayer (17) showed that the reduction in entropy for the condition that the ends of a linear chain of N segments are to lie in the same plane or on one side of a plane is proportional to ln N. Therefore, the assumption that the backfolding of the middle block in the micelle follows the same functional form is made. Hence, the backfolding or looping entropy makes the following contribution in the case of a BAB copolymer:

$$\frac{(\Delta\mu_g^0)_{\text{loop}}}{kT} = \frac{3}{2}\,\beta\,\ln[N_{\text{A}}]. \qquad [18]$$

Here, β is an excluded volume parameter which is equal to unity when the excluded volume effects are negligible and larger than unity when these effects become important. In the present calculations, β is taken to be unity.

4. MODEL PREDICTIONS AND CONCLUSIONS

To perform quantitative calculations, the values of molecular constants appearing in Eqs. [8] to [18] are needed for PEO–PPO diblock and PEO–PPO–PEO triblock copolymers, solvent water, and hydrocarbon solubilizates. The molecular volumes v_J of the solubilizates, their solubility parameters δ_J, and the interfacial tensions σ_{JW} between water and the solubilizates are listed in Table 1. The Flory interaction parameters χ_{AJ} are estimated using the solubility parameters δ_A and δ_J as indicated in Section 2. The Flory interaction parameters χ_{AW} and χ_{BW} have been estimated to be 2.1 and 0.2, respectively, based on available activity data on aqueous

TABLE 3

Predicted Core Radius, Corona Thickness, Aggregation Number, Solubilization Capacity, and CMC of $E_{200}P_{64}$ Diblock Copolymer Micelles at 25°C

Solubilizate	R (Å)	D (Å)	g	η^a	$-\ln X_{\text{CMC}}$
Benzene	92.7	135	279	0.478 (0.51)	64.3
Toluene	83.3	132	235	0.393 (0.40)	58.3
o-Xylene	79.4	131	216	0.357 (0.33)	56.0
Ethyl benzene	76.2	130	203	0.316 (0.41)	54.6
Cyclohexane	69.8	128	180	0.211 (0.18)	52.5
Hexane	58.1	120	122	0.069 (0.08)	48.3
Heptane	57.2	120	119	0.057 (0.08)	47.8
Octane	57.0	119	117	0.053 (0.08)	47.6
Decane	55.7	118	112	0.036 (0.06)	47.2
None	53.2	116	101	—	46.6

^{a} Values in parentheses are experimental data from Ref. (4) summarized in Table 1.

solutions of PEO and PPO (8). The molecular volumes of the segments are $v_A = 96.5$ Å^3 (for PO) and $v_B = 64.6$ Å^3 (for EO) while for water, $v_W = 30$ Å^3. Since the molecular weights of the segments are 58 for PO and 44 for EO, the block copolymer of total molecular weight 12,500 with 30 wt% propylene oxide employed in our experiments (4) contains approximately 200 ethylene oxide segments and 64 propylene oxide segments. All predictive calculations for the diblock and triblock copolymers have concentrated on these numbers of EO and PO segments. The predicted micellar structural properties are summarized in Tables 3 to 5 for three block copolymer systems. The various contributions to the free energy of solubilization corresponding to the equilibrium aggregate are listed in Tables 6 to 8 for the same three block copolymer systems.

The predictions based on the uniform concentration–nonuniform deformation model are summarized in Table 3 for $E_{200}P_{64}$ diblock copolymer micelles. Also shown within the parentheses are the measured solubilization capacities (from Table 1) expressed as volume fractions in the micelle core. In general, the agreement between the experimental and measured values of η is reasonably satisfactory for all the solubilizates. Whereas the theory permits the prediction of all the structural features of the micelles such as g, R, D and the CMC, experimental data for these variables are currently not available and hence the corresponding comparisons have not been possible. The predicted results show that the solubilization capacity is larger when the core block A–solubilizate J interactions are favorable (small χ_{AJ}), the solubilizate–solvent interfacial tension (σ_{JW}) is lower, and the molecular volume of the solubilizate (v_J) is smaller. Consequently, the aromatic molecules are found to display a larger solubilization limit compared with the aliphatic molecules. Solubilization is found to increase the micellar core

TABLE 4

Predicted Core Radius, Corona Thickness, Aggregation Number, Solubilization Capacity, and CMC of $E_{100}P_{64}E_{100}$ Triblock Copolymer Micelles at 25°C

Solubilizate	R (Å)	D (Å)	g	η^a	$-\ln X_{CMC}$
Benzene	55.2	77.1	72	0.366 (0.51)	37.2
Toluene	50.2	75.7	61	0.279 (0.40)	32.0
o-Xylene	48.3	75.0	57	0.245 (0.33)	30.1
Ethyl benzene	46.7	74.5	54	0.208 (0.41)	29.0
Cyclohexane	43.7	73.7	49	0.124 (0.18)	27.2
Hexane	39.3	71.0	39	0.039 (0.08)	24.5
Heptane	38.9	70.8	38	0.031 (0.08)	24.2
Octane	38.7	70.7	38	0.027 (0.08)	24.1
Decane	38.2	70.3	37	0.016 (0.06)	23.8
None	37.4	69.8	35	—	23.5

^{a} Values in parentheses are experimental data from Ref. (4) summarized in Table 1.

radius and decrease the CMC. The larger the solubilization capacity, the more significant are the changes in R and the CMC. The increase in the core radius R results not only from the incorporation of the solubilizate [as was assumed in Ref. (10) while interpreting the experimental data], but also because of the increasing number of block copolymer molecules that are accommodated within a micelle. This increase in g is more dramatic in the case of solubilizates whose uptake by the micelles is large. In comparison, the corona thickness D is not very much affected by solubilization.

Table 4 lists the predicted results for $E_{100}P_{64}E_{100}$ triblock copolymer in water at 25°C. A comparison with the results for diblock copolymer $E_{200}P_{64}$ of the same molecular weight and composition (presented in Table 3) shows that the micellar core radius R, aggregation number g, shell thickness

TABLE 5

Predicted Core Radius, Corona Thickness, Aggregation Number, Solubilization Capacity, and CMC of $E_{100}P_{32}$ Diblock Copolymer Micelles at 25°C

Solubilizate	R (Å)	D (Å)	g	η^a	$-\ln X_{CMC}$
Benzene	55.2	77.1	144	0.366 (0.51)	34.5
Toluene	50.2	75.7	122	0.279 (0.40)	32.0
o-Xylene	48.3	75.0	114	0.245 (0.33)	31.0
Ethyl benzene	46.7	74.5	108	0.208 (0.41)	30.4
Cyclohexane	43.7	73.7	98	0.124 (0.18)	29.5
Hexane	39.3	71.0	78	0.039 (0.08)	28.2
Heptane	38.9	70.8	76	0.031 (0.08)	28.1
Octane	38.7	70.7	76	0.027 (0.08)	28.0
Decane	38.2	70.3	74	0.016 (0.06)	27.8
None	37.4	69.8	70	—	27.7

^{a} Values in parentheses are experimental data from Ref. (4) summarized in Table 1.

TABLE 6

Calculated Contributions to the Standard Free Energy Change on Aggregation (in kT) for $E_{200}P_{64}$ Diblock Copolymer Micelles at 25°C

Solubilizate	$(\Delta\mu_g^0)_{A,def}$	$(\Delta\mu_g^0)_{A,dil}$	$(\Delta\mu_g^0)_{B,def} + (\Delta\mu_g^0)_{B,dil}$	$(\Delta\mu_g^0)_{int}$	$(\Delta\mu_g^0)_{loc}$
Benzene	1.87	−116.10	17.56	27.63	4.74
Toluene	1.42	−108.26	17.20	26.53	4.79
o-Xylene	1.24	−104.87	16.89	25.94	4.81
Ethyl benzene	1.11	−103.03	16.80	25.65	4.83
Cyclohexane	0.86	−100.12	16.72	25.17	4.89
Hexane	0.45	−91.19	14.82	22.70	4.94
Heptane	0.42	−90.39	14.67	22.51	4.94
Octane	0.41	−90.07	14.62	22.46	4.95
Decane	0.37	−89.04	14.38	22.17	4.95
None	0.30	−87.23	13.87	21.57	4.96

D, and solubilization capacities η are all considerably smaller for the case of triblock copolymer compared with diblock copolymer. The CMCs are significantly larger for the triblock copolymer compared with the diblock copolymer. The measured η (shown in parentheses) are in poorer agreement with the predictions for the triblock copolymer micelles compared with the diblock copolymer micelles.

In Tables 6 to 8, the various free energy contributions to solubilization of hydrocarbons in the three block copolymer micellar systems are summarized. All the free energies correspond to spherical aggregates favored at equilibrium whose dimensions have been specified in Tables 3 to 5. The contribution from the dilution of A block (including the swelling of the core by the solubilizate) is negative and is responsible for the occurrence of solubilization. All other free energy contributions are positive. Of these, the free energy of localization has only a weak dependence on the aggregation num-

TABLE 7

Calculated Contributions to the Standard Free Energy Change on Aggregation (in kT) for $E_{100}P_{64}E_{100}$ Triblock Copolymer Micelles at 25°C^a

Solubilizate	$(\Delta\mu_g^0)_{A,def}$	$(\Delta\mu_g^0)_{A,dil}$	$(\Delta\mu_g^0)_{B,def} + (\Delta\mu_g^0)_{B,dil}$	$(\Delta\mu_g^0)_{int}$	$(\Delta\mu_g^0)_{loc}$
Benzene	2.84	−112.01	20.13	36.93	8.29
Toluene	2.28	−104.46	19.63	35.49	8.37
o-Xylene	2.06	−101.32	19.28	34.79	8.40
Ethyl benzene	1.9	−99.52	19.14	34.39	8.44
Cyclohexane	1.60	−96.59	18.92	33.69	8.51
Hexane	1.21	−90.05	17.45	31.62	8.56
Heptane	1.17	−89.36	17.31	31.42	8.57
Octane	1.16	−89.04	17.24	31.33	8.57
Decane	1.11	−88.27	17.05	31.07	8.58
None	1.05	−87.23	16.75	30.68	8.58

^{a} Free energy contribution from the backfolding of A block is a constant independent of the presence or absence of solubilizates and has the magnitude of 6.25 kT.

ber and on the nature of the solubilizate; thus it has negligible effect on the microstructural parameters. Similarly, the free energy contribution associated with looping of the A block in the triblock copolymer is a constant and has no influence on the structural parameters. Both of these contributions, however, affect the CMC. In contrast, the contributions associated with the corona block B and the formation of the micellar core-shell interface are dominant over the other positive free energy contributions and influence all the structural characteristics of micelles.

The differing results obtained for the $E_{200}P_{64}$ diblock and the $E_{100}P_{64}E_{100}$ triblock copolymers can be understood on the basis of the free energy model developed. First, for the BAB triblock copolymers (where B refers to the hydrophilic and A to the hydrophobic blocks), the A blocks are subjected to backfolding so as to exclude the B blocks from the micellar core. This looping free energy contribution is a positive constant dependent on the block copolymer molecular weight and composition but independent of micellar size characteristics. Hence, its only effect is to increase the CMC in the case of triblock copolymers compared with diblock copolymers of identical molecular weight and composition. In other words, it is more difficult to form micelles with triblock copolymers than with their diblock counterparts. Secondly, in the case of a triblock copolymer, the backfolded A block in the micellar core is treated as being equivalent to two A chains of half the molecular weight. Also, each B block of the triblock copolymer has half the molecular weight when compared with the B block of a diblock copolymer of same overall molecular weight and composition. Consequently, the aggregation number, core radius, corona thickness, and volume fraction of solubilizate in the micelle core are all appreciably smaller for triblock copolymer micelles when compared with micelles of diblock copolymer having identical molecular weight and composition.

From what has been mentioned above, one can anticipate that a triblock copolymer behavior is practically equivalent to a diblock copolymer having the same composition but half its molecular weight in many respects. Indeed, the core radius, corona thickness, and volume fraction solubilizate are identical for a triblock copolymer micelle and a micelle of diblock copolymers having the same composition but half the molecular weight. This is seen from the results summarized in Table 5 for $E_{100}P_{32}$. Since the core radii are equal, from geometrical relations one gets an aggregation number that is twice as large for these diblock copolymer micelles compared with the $E_{100}P_{64}E_{100}$ triblock copolymer micelles. In addition to the structural features being comparable, one can observe that the CMCs are not very significantly different in the two cases despite the vast difference in the sizes of the A blocks. This is because of the compensation provided by the corona free energy, interfacial free energy, and looping free energy contributions (see Tables 7 and 8). From

TABLE 8

Calculated Contributions to the Standard Free Energy Change on Aggregation (in kT) for $E_{100}P_{32}$ Diblock Copolymer Micelles at 25°C

Solubilizate	$(\Delta\mu_g^0)_{A,def}$	$(\Delta\mu_g^0)_{A,dil}$	$(\Delta\mu_g^0)_{B,def}$ $+ (\Delta\mu_g^0)_{B,dil}$	$(\Delta\mu_g^0)_{int}$	$(\Delta\mu_g^0)_{loc}$
Benzene	1.38	−68.81	10.39	18.46	4.14
Toluene	1.09	−65.04	10.15	17.75	4.19
o-Xylene	0.99	−63.47	9.98	17.40	4.20
Ethyl benzene	0.91	−62.57	9.91	17.20	4.22
Cyclohexane	0.76	−61.10	9.80	16.85	4.25
Hexane	0.56	−57.83	9.07	15.81	4.28
Heptane	0.54	−57.49	8.99	15.71	4.28
Octane	0.51	−57.33	8.96	15.66	4.28
Decane	0.49	−56.94	8.86	15.53	4.29
None	0.48	−56.42	8.70	15.34	4.29

the free energy expressions (Eqs. [8] to [18]) one can clearly observe that if N_A/q and N_B/q are identical for a diblock molecule and a symmetric triblock molecule, then the expressions for the free energy of solubilization are identical (except for a constant term) for the aggregates formed of these two kinds of molecules, for the same values for R, D, η, and a/q. Therefore, the free energy minimization yields the same values of these structural parameters for the $E_{100}P_{64}E_{100}$ triblock and $E_{100}P_{32}$ diblock copolymer micelles. The geometrical relation for a spherical aggregate in conjunction with the molecular packing requirement then dictates that the aggregation number of the diblock $E_{100}P_{32}$ micelle will be twice that of the triblock $E_{100}P_{64}E_{100}$ micelle.

The quantitative prediction of aggregate characteristics discussed above is influenced by the simplifying assumptions that have been made in constructing the model. For example, only approximate estimates for the interfacial tension σ_{agg} characteristic of the hydrophobic core–hydrophilic corona interface are employed in the present calculations. To obtain improved estimates of σ_{agg}, future developments in the treatment of a constrained interface between two solutions are necessary. The model presented here assumes a sharp interface and does not allow the penetration of water or of the hydrophilic block into the hydrophobic core. It is of interest to relax this assumption and examine how the model predictions will be modified for the case of a diffuse interface. For solubilizates such as benzene, which are also good solvents for PEO, there is the possibility that in addition to the solubilizate being present in the micellar core, it could also be present in the micellar shell. The model presented here does not describe such a situation. The presence of any solubilizate in the micellar shell can alter the predicted micellar dimensions and the solubilization capacity.

The main advantage of the present theory is that it allows the prediction of all the microstructural features of micelles

containing solubilizates with only minor computational efforts. Another advantage of the theory is that all free energy contributions are given as explicit analytical functions directly linked to physicochemical changes accompanying micellization and solubilization, and involving only molecular constants and geometrical variables. We believe that more detailed measurements of various microstructural characteristics of micelles are essential for meaningful future developments in the theory of solubilization.

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