

Measurement and Prediction of Ionic/Nonionic Mixed Micelle Formation and Growth

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We investigate synergism in mixed micelle formation and growth in two ionic/nonionic surfactant mixtures. In one mixture, the nonionic surfactant dodecyl hexa(ethylene oxide), or $C_{12}E_6$, is mixed with the ionic surfactant sodium dodecyl sulfate, or SDS. In the other mixture, $C_{12}E_6$ is mixed with sodium dodecyl hexa(ethylene oxide) sulfate, or SDE_6S . The SDE_6S head, which contains six ethylene oxide units and a sulfate group, "interpolates" between $C_{12}E_6$ and SDS and allows us to investigate in detail the effects of electrostatic and steric interactions between the surfactant heads on mixed micelle formation and growth. For both surfactant mixtures, we measure the critical micelle concentration (cmc) as a function of solution composition, and we use static light scattering to measure the weight-average mixed micelle aggregation number as a function of both solution composition and total surfactant concentration. The analysis of the light scattering data accounts for both micelle growth and intermicellar interactions. We also infer the mixed micelle shape and hydration with combined static and dynamic light scattering measurements, and we qualitatively confirm the trends of micelle size as a function of solution composition with independent measurements of relative viscosity. The experimental mixture cmc and mixed micelle aggregation numbers compare well with those predicted by a recently developed molecular-thermodynamic theory of mixed micellization. The theory also permits a detailed analysis of the interplay of electrostatic and steric interactions affecting the formation and growth of mixed micelles in each surfactant mixture.

I. Introduction

Mixtures of ionic and nonionic surfactants are commonly used in many practical surfactant applications because the solution behaviors of these surfactants can be complementary. For example, in laundry detergent formulations, anionic surfactants are used to maximize solubilization, while nonionic surfactants are used to maximize water hardness tolerance.¹ From a fundamental point of view, mixtures of ionic and nonionic surfactants are interesting because they often exhibit highly nonideal behavior. The addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsions between the charged surfactant heads and greatly facilitate mixed micelle formation. The nonideal behavior of an ionic/nonionic surfactant mixture can also be influenced by other structural characteristics of the two surfactants, such as differences in the sizes of the surfactant heads or the lengths of the surfactant tails.

It is useful to fundamentally understand how the molecular structures of surfactants in a surfactant mixture affect the solution properties of the mixture, such as the mixture critical micelle concentration (cmc) and the size and shape of the mixed micelles. Practically, this type of understanding can help in choosing surfactant structures which will result in the desired performance properties. To better characterize the relationship between the structures of surfactants in ionic/nonionic surfactant mixtures and their solution properties, in this paper, we experimentally and theoretically investigate both micelle formation and micelle growth in two aqueous ionic/nonionic mixed surfactant systems. By comparing the experimental mixture cmc's and micelle sizes with theo-

retical predictions of these quantities, we relate the experimental behavior to the surfactant molecular structures.

The surfactant mixtures that we have chosen to study include a member of a family of surfactants known as alkyl poly(ethylene oxide) sulfates. In these surfactants, the charged sulfate group is separated from the alkyl tail by a variable number of ethylene oxide (EO) units. Although these surfactants are ionic, increasing the number of EO units distances the charge from the tail and reduces their ionic character. In this study, sodium dodecyl hexa(ethylene oxide) sulfate, or SDE_6S , is mixed with the nonionic surfactant dodecyl hexa(ethylene oxide), or $C_{12}E_6$, and the behavior of this mixture is compared with that of a mixture of sodium dodecyl sulfate (SDS) and $C_{12}E_6$. In the $SDE_6S/C_{12}E_6$ mixture, both surfactants have the same number of EO groups. Therefore, sterically, their mixing behavior should be ideal, and this pair allows us to isolate the electrostatic contribution to mixed micellization. We chose to contrast the behavior of $SDE_6S/C_{12}E_6$ mixtures with that of $SDS/C_{12}E_6$ mixtures, to specifically isolate the effect of the EO groups, and thus study the steric contribution to mixed micelle formation.

$SDS/C_{12}E_6$ mixtures have been previously studied by several experimental techniques and analyzed by various theoretical approaches. Surface tension^{2,3} and neutron scattering² techniques were respectively used to measure the mixture cmc and the micelle composition of $SDS/C_{12}E_6$ mixed micelles in aqueous solutions. The experimental measurements were analyzed with regular solution theory.⁴ Although regular solution theory described the experimental measurements well, it is not predictive, and because it does not consider the molecular structures of

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the surfactants explicitly, it cannot give detailed insight into the mixture properties at a molecular level. Titration calorimetry³ was also used to measure the enthalpy of forming mixed micelles, indicating that regular solution theory, which assumes that the excess entropy of forming a mixed micelle is zero, does not describe mixed micelle formation well. Electron spin-echo modulation⁵ measurements of SDS/C₁₂E₆ mixed micelles were contrasted with those of dodecyltrimethylammonium bromide (DTAB), also mixed with C₁₂E₆. This technique gives detailed information on the micellar structure, indicating that the SDS heads are less deeply embedded in the ethylene oxide head layer than the DTAB heads, perhaps reflecting specific interactions. The aggregation numbers of SDS/C₁₂E₆ mixed micelles at a single total surfactant concentration were measured using static light scattering and were compared with those predicted by a theory⁶ that depended on knowing the micelle composition. Finally, cloud-point measurements⁷ were used to study the effect of SDS on the phase separation of aqueous solutions of C₁₂E₆. Very small amounts of SDS caused significant increases in the cloud-point temperatures. The results were explained in terms of repulsive electrostatic intermicellar interactions. While these studies yielded useful information on the solution behavior of SDS/C₁₂E₆ mixtures, they did not provide the complete set of experimental measurements that we desire nor did they explain the observed experimental results at the molecular level.

In contrast to SDS/C₁₂E₆ mixtures, SDE₆S/C₁₂E₆ mixtures have not been previously studied. Other members of the alkyl poly(ethylene oxide) sulfate family, containing one and three EO groups, have been mixed with the nonionic surfactant decyl methyl sulfoxide and studied⁸ with surface tension measurements. The authors found⁸ that synergistic interactions between the anionic and nonionic surfactants weakened as the length of the EO chain increased, but their regular solution theory analysis did not consider the detailed surfactant molecular structures. In a separate study, an alkyl poly(ethylene oxide) sulfate with a distribution of EO groups was mixed with the cationic surfactant tetradecyl trimethylammonium bromide and studied⁹ by surface tension, interfacial tension, and cloud-point measurements. The anionic/cationic surfactant mixture was proposed to form a soluble complex and to behave as a "pseudo-nonionic" surfactant. Again, while these studies are valuable, they do not provide a comprehensive set of experimental data, and they lack a molecular-level explanation of the observed experimental results.

The work presented in this paper differs from previous studies on these types of mixed surfactant systems in that we simultaneously study the formation of mixed micelles as well as their size and shape in both surfactant mixtures, rather than focusing exclusively on micelle formation^{2,3,8,10} or on micelle growth.⁶ We initially characterize both surfactant mixtures by measuring the mixture cmc as a function of solution composition. We next measure the size and shape of the mixed micelles as a function of solution composition and total surfactant concentration

using static and dynamic light scattering. In studying the growth of mixed micelles, we account for and analyze the effect of intermicellar interactions, an aspect of micelle growth that is often neglected in analyzing mixed surfactant systems. In determining the micelle shape, we also calculate the hydration of the ethylene oxide groups in these surfactants. The micelle size and shape determined by light scattering is then qualitatively verified with independent viscosity measurements. Together, all these measurements provide us with a thorough characterization of mixed micelle formation and growth in a relatively dilute regime. To explain the behavior that we observe, we compare the experimental measurements of the mixture cmc and the mixed micelle aggregation numbers with predictions of these properties by a recently developed molecular-thermodynamic theory for mixed surfactant systems.¹¹⁻¹⁴ In addition to predicting the mixture cmc and the mixed micelle aggregation numbers for these surfactant mixtures, the theory allows us to analyze the observed experimental behavior in terms of the free-energy contributions to mixed micelle formation and growth. This analysis provides a quantitative, molecular-level understanding of the intramicellar surfactant interactions contributing to mixed micelle formation and growth.

The three surfactants examined have dodecyl hydrocarbon tails, so that interactions within the mixed micelles that they form are due only to differences in the structures of the surfactant heads. We specifically study several aspects of the relationship between the surfactant molecular structures and their micellar solution properties. First, we identify the effect of the EO groups in SDE₆S on mixed micelle formation and growth in the SDE₆S/C₁₂E₆ system, as compared to the SDS/C₁₂E₆ system. Second, by comparing experimental measurements with theoretical predictions, we infer the conformation of the EO groups in SDE₆S, since they could be either fully extended or more globular. An extended conformation would maximize the distance from the micellar core/water interface to the surface of charge, thus reducing the electrostatic repulsions between the charged SDE₆S heads, but would be entropically unfavorable from a conformational viewpoint. Third, we identify the dominating intramicellar interactions in mixed micelle formation at the cmc, when micelles first form, and contrast them with those affecting micelle growth at higher surfactant concentrations.

The remainder of the paper is organized as follows. In section II, we describe the surfactants and the experimental methods used to determine the cmc of the mixed micellar solutions and the aggregation numbers of the mixed micelles. We also describe the intermicellar interactions that must be accounted for in analyzing the light scattering measurements. The molecular-thermodynamic theory which is used to predict the surfactant solution properties and to analyze the contributions to mixed micelle formation and growth is briefly described in section III. In section IV, we present the experimental measurements and compare them with the theoretical predictions. Finally, in section V, we present concluding remarks.

II. Materials and Experimental Methods

A. Materials. The nonionic surfactant C₁₂E₆ (lot 4023) was obtained from Nikko Chemicals, Tokyo, and due to

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its high purity, as indicated by the absence of a minimum in the surface tension–surfactant concentration curve, was used as received. The ionic surfactant SDS was purchased from Sigma, St. Louis, MO (>99% pure), and since a minimum was observed in its surface tension–surfactant concentration curve, it was purified by recrystallization three times from an ethanol/water mixture. The ionic surfactant SDE₆S was synthesized by Witco Corp. for this study by sulfating C₁₂E₆ (lot 4023) from Nikko. This procedure guaranteed that both the hydrocarbon tail and the ethylene oxide groups in the SDE₆S head were monodisperse and the same as in C₁₂E₆. The SDE₆S was 95.2% pure and contained 1.2% unsulfated nonionic surfactant, and 3.6% salt, mainly Na₂SO₄.

For the light scattering measurements, SDE₆S was used as received. These measurements were performed in aqueous 0.1 M sodium chloride (NaCl) solutions, in which the salt concentration was high enough to make the effect of the salt impurities in SDE₆S negligible. For the cmc measurements, the SDE₆S was purified¹⁵ by reverse phase liquid chromatography using a SEP-Pak C18 cartridge (Waters Assoc., Milford, MA). The cmc measurements were performed in aqueous solution, in which the salt impurities in SDE₆S could greatly affect the solution properties. Note that in this purification procedure, the surfactant solution was diluted such that the total surfactant concentration was below the expected cmc of SDE₆S, to ensure that surface-active impurities could not be solubilized in surfactant micelles. After the dilute solution was passed through the cartridge, the pure surfactant was recovered by lyophilization. The purity of SDS and SDE₆S after these purification procedures was verified by the absence of a minimum in their individual surface tension–surfactant concentration curves.

B. Sample Preparation. All solutions were aqueous and were prepared using deionized water which had been further purified by a Milli-Q ion exchange system. All glassware was cleaned before use by soaking in a 1 N NaOH–ethanol bath for at least 8 h, followed by soaking in a 1 N nitric acid bath for at least another 8 h. The glassware was then thoroughly rinsed with Milli-Q water and dried in an oven.

Solutions for surface tension measurements were prepared at different surfactant concentrations by volumetrically diluting an aqueous stock solution. The stock solution was made by dissolving the amount of each surfactant required for the desired solution composition in Milli-Q water and stirring well. All solutions were used within 48 h of their preparation.

All solutions for static and dynamic light scattering measurements were made in an aqueous 0.1 M NaCl solution. Sodium chloride (Mallinckrodt, reagent grade) was roasted overnight at 450 °C before solutions containing salt were prepared, to evaporate any associated water. Solutions of a single solution composition were made at different surfactant concentrations by diluting a stock solution with an aqueous 0.1 M NaCl solution by weight. The stock solution was made by dissolving the amount of each surfactant required for the desired solution composition in an aqueous 0.1 M NaCl solution. Solutions at a single surfactant concentration, but at different solution compositions, were made by mixing the appropriate amounts of stock solutions of each of the two single surfactants at the same concentration. All solutions were filtered once through a 0.02 μm filter (Whatman, Anotop) directly into a cylindrical scattering cell and sealed

until use. Repeated filtering was unnecessary due to the small filter pore size. The same stock solutions prepared for the light scattering measurements were also used for the viscosity measurements. To measure viscosities at different concentrations, dilutions were made directly in the viscometer with an aqueous 0.1 M NaCl solution.

C. Experimental Measurements. 1. Critical Micelle Concentration. The critical micelle concentration (cmc) was determined for surfactant mixtures of various solution compositions by the surface tension method using a Wilhelmy plate tensiometer (Kruss K10T). This method is based on the fact that below the cmc, the surface tension decreases rapidly with increasing surfactant concentration, while above the cmc, any change in surface tension with increasing surfactant concentration is much more gradual. The surface tension of a mixed surfactant solution of a given composition was measured as a function of the total surfactant concentration. The cmc was identified as the break point in a plot of surface tension versus log(surfactant concentration), with linear regions both below and above the cmc. All measurements were made in aqueous solutions at 25 °C. Each measurement was repeated at least three times. The typical error in the surface tension measurement was less than 1%, and the typical error in the cmc value was less than 5%.

2. Static Light Scattering. Apparent weight-average micelle molecular weights were determined by static light scattering (SLS). The total intensity of scattered light was measured using a 2 W argon laser (Lexel model 95) at a wavelength of $\lambda = 514.5$ nm. The apparatus also included a BI-200SM goniometer system (Brookhaven Instrument Co., Holtsville, NY), and a photomultiplier tube which could be moved circularly around the sample holder. The sample temperature was kept at 25 °C with a circulating ethylene glycol bath. All measurements were made at a scattering angle of $\theta = 90^\circ$ after initial studies indicated that the micelles were too small to exhibit significant angular dependence of the scattered light. The intensity of scattered light was measured at least four times for each sample. The average error in these repeated measurements was approximately 2%.

The Rayleigh ratio at an angle θ , R_θ , was calculated based on the intensity of scattered light from the micellar solution and from a reference solvent, such that¹⁶

$$R_\theta = \frac{\langle I(\theta) \rangle}{\langle I_{\text{ref}}(\theta) \rangle} R_{\text{ref}}(\theta) \left(\frac{n}{n_{\text{ref}}} \right)^2 - R_\theta^\circ \quad (1)$$

where $\langle I(\theta) \rangle$ and $\langle I_{\text{ref}}(\theta) \rangle$ are the average intensities of scattered light from the micellar solution and from the reference solvent, respectively, $R_{\text{ref}}(\theta)$ is the Rayleigh ratio of the reference solvent, n and n_{ref} are the refractive indices of the solution and of the reference solvent, respectively, and R_θ° is the Rayleigh ratio of the salt solution in the absence of micelles. Toluene was used as the reference solvent, with $R_{\text{ref}}(\theta) = 3.20 \times 10^{-5} \text{ cm}^{-1}$ (ref 17) and $n_{\text{ref}} = 1.505$ at 25 °C.¹⁸

In general, the difference in Rayleigh ratio between the micellar solution and the salt solution in the absence of micelles, $\Delta R_\theta = R_\theta - R_\theta^\circ$, is related to M_{app} , the apparent

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molecular weight of the micelles, by^{19,20}

$$\frac{K_0(c - \text{cmc})}{\Delta R_\theta} = \frac{1}{M_{\text{app}}} \quad (2)$$

with the optical constant K_0 given by¹⁹

$$K_0 = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4} \quad (3)$$

where n_0 is the refractive index of the salt solution in the absence of micelles, dn/dc is the refractive index increment of the solution, N_A is Avogadro's number, and λ is the wavelength of light. In eq 2, c is the total surfactant concentration, but for all the micellar solutions examined, $c \gg \text{cmc}$, so that the micelle concentration $c - \text{cmc} \approx c$. Note that M_{app} is an apparent molecular weight and includes the effect of any intermicellar interactions. Note also that for polydisperse solutions, M_{app} is the apparent weight-average molecular weight.

Experimentally, we determined M_{app} for each sample by measuring $K_0/\Delta R_\theta$ and applying eq 2. For surfactant mixtures which form a single type of mixed micelle (as opposed, for example, to mixtures of hydrocarbon and fluorocarbon surfactants, which could form two micelle populations), the scattered light intensity depends on the sum of the contributions from each surfactant in the mixed micelle, weighted by its refractive index increment.²¹ The optical constant in eq 3, K_0 , is then modified such that

$$K_0 = \frac{4\pi^2 n_0^2}{N_A \lambda^4} \left[\alpha_A^w \left(\frac{dn}{dc} \right)_A + \alpha_B^w \left(\frac{dn}{dc} \right)_B \right]^2 \quad (4)$$

where α_A^w and α_B^w are the weight fractions of surfactants A and B in the mixed micelle, respectively, and $(dn/dc)_A$ and $(dn/dc)_B$ are the refractive index increments of solutions of surfactants A and B, respectively. This approach is similar to that for diblock copolymers,²² in which the refractive index increment of the polymer is related to the weight average of the refractive index increments of the polymers composing the diblock. An alternative approach^{17,23} is to substitute $(dn/dc)_\alpha$, the refractive index increment measured for a mixed micellar solution of composition α , for (dn/dc) in eq 3. Because K_0 depends on the square of the refractive index increment, it is very sensitive to the value of (dn/dc) . For several cases that we tested, using $(dn/dc)_\alpha$ in eq 3 instead of using eq 4 gave different results, and for mixed micelles, according to ref 21, eq 4 provides the more systematic expression.

The refractive index increment was determined for each of the three pure surfactant solutions in 0.1 M NaCl at 25 °C using an Abbe refractometer. The increment was calculated by fitting n as a function of concentration to a linear function. The values of dn/dc for each surfactant are listed in Table 1. The value for C_{12}E_6 agrees well with that measured previously²⁴ in water at 25 °C. The

Table 1. Refractive Index Increment for Aqueous Surfactant Solutions in 0.1 M NaCl

surfactant	dn/dc at 25 °C (mL/g)
C_{12}E_6	0.139
SDS	0.108
SDE_6S	0.130

increment for SDS is also reasonably consistent with a previously measured²⁵ value in water at 23 °C. The increment for SDE_6S lies between those of C_{12}E_6 and SDS and is similar to the refractive index increment for SDE_4S measured²⁶ under the same solution conditions.

The apparent molecular weight of the mixed micelle depends both on the actual mixed micelle molecular weight and on the intermicellar interactions. To determine the actual molecular weight of the mixed micelle, M , from the apparent molecular weight, M_{app} , the intermicellar interactions were accounted for as will be described in section II.D.1 below.

3. Dynamic Light Scattering. The average diffusion coefficient of the micelles was measured by dynamic or quasielastic light scattering (QLS). All measurements were performed at 25 °C at a scattering angle of $\theta = 90^\circ$, using the apparatus described in section II.C.2. The autocorrelation function was obtained using a digital correlator (BI 9000 AT, Brookhaven Instruments, Holtsville, NY) with linearly spaced channels. The collective diffusion coefficient, D_c , was determined from the measured correlation function using the second cumulant in the cumulant expansion method.²⁷ The diffusion coefficient was measured at least three times for each sample. The average error in these measurements was approximately 4%. Since the collective diffusion coefficient, D_c , reflects both the average size of the micelle as well as the intermicellar interactions, D_c and the corresponding hydrodynamic radius were corrected for intermicellar interactions as will be described in section II.D.2 below.

4. Viscosity. The kinematic viscosities of the mixed surfactant solutions were measured using Cannon-Ubbelohde capillary viscometers immersed in a water bath having a temperature stability of ± 0.01 °C. All measurements were performed at 25 °C. The time for a surfactant solution to flow through the capillary was measured to the nearest 0.1 s and was converted to kinematic viscosity values using the calibration constant of the viscometer. The viscosity of a sample was measured at least four times. The typical error in these measurements was less than 3%. The viscosity was measured as a function of total surfactant concentration for mixed surfactant solutions of a given composition by diluting a concentrated solution with an aqueous 0.1 M NaCl solution sequentially by volume directly in the viscometer. The relative viscosity, η_r , was calculated by dividing the kinematic viscosity of a sample, η , by the viscosity of the aqueous 0.1 M NaCl solution, η_0 .

D. Analysis of Intermicellar Interactions. 1. Micelle Aggregation Numbers. The intensity of scattered light depends both on the molecular weight of the micelles and on the intermicellar interactions. The deconvolution of these two effects is simplified under some circumstances. For example, if the intermicellar interactions are weak and can be neglected, the intensity of scattered light can be directly related to the molecular weight of the micelles to determine micelle growth at various concentrations. This is the case in mixtures of

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nonionic or zwitterionic surfactants at relatively low surfactant concentrations.^{28–30} These micelles are not charged and, therefore, do not exhibit strong electrostatic interactions, and the surfactant concentration is low enough that repulsive, excluded-volume interactions, and attractive interactions can be neglected. Conversely, if the micelle size does not change with increasing surfactant concentration, as in the case of pure ionic surfactants^{31,32} or mixtures of ionic surfactants³³ in aqueous solution, the micelle size can be determined by extrapolating the SLS data to the cmc, where the intermicellar interactions are negligible.

In the SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed surfactant systems, neither of these simplifications is possible. The ionic/nonionic mixed micelles formed by SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ are partially charged and, therefore, experience repulsive electrostatic intermicellar interactions. At the low surfactant concentrations and temperatures at which we performed our measurements, attractive intermicellar interactions are negligible,^{26,28–30} because they are generally important only at higher surfactant concentrations or at higher solution temperatures. However, repulsive electrostatic interactions are longer ranged and are less sensitive to temperature and can therefore be important even at the solution conditions considered here. Note that excluded-volume interactions are inherently included when the repulsive electrostatic intermicellar interactions are accounted for (see eq 11 below).

While the intermicellar interactions cannot be neglected, neither can the micelle growth in the SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ surfactant mixtures be neglected. At low ionic micelle compositions, where the intramicellar electrostatic interactions between charged surfactant heads are relatively weak, the mixed micelles can exhibit growth with increasing total surfactant concentration, similar to the growth that is common in some alkyl poly(ethylene oxide) surfactants, such as C₁₂E₆.^{12,28,34} Therefore, in analysis of SLS data, both the changing molecular weight of the mixed micelles with total surfactant concentration and the intermicellar interactions must be simultaneously considered. Previous SLS studies of mixed micelles either have ignored the change in micelle size with total surfactant concentration and have extrapolated the data to the cmc⁶ or have reported *apparent* micelle molecular weights,^{35,36} in which the intermicellar interactions are neglected. Here, we use SLS in a manner that accounts both for the growth of the mixed micelles and for their intermicellar interactions. The Rayleigh ratio, $\Delta \mathcal{R}_\theta$, can be written as^{19,20}

$$\Delta \mathcal{R}_\theta = K_0(c - \text{cmc})MP(Q)S(Q) \quad (5)$$

where M is the weight-average micelle molecular weight, $P(Q)$ is the particle form factor, reflecting intramicellar interactions, and $S(Q)$ is the static structure factor,

reflecting intermicellar interactions. The scattering vector, Q , has a magnitude given by

$$Q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \quad (6)$$

If the particle size is much smaller than the wavelength of light, as we expect for the micelles formed by these surfactant mixtures, then $P(Q)$ has a value of unity. In addition, in this limit, the structure factor is not sensitive to the angle of scattered light, and $S(Q) \approx S(0)$, the structure factor in the limit when $Q \rightarrow 0$. Note that for polydisperse solutions, in eq 5, M is the weight-average molecular weight, and $P(Q)$ and $S(Q)$ represent average particle form factors and static structure factors, respectively.

In the limit when $Q \rightarrow 0$, the optical constant, K_0 , the Rayleigh ratio, $\Delta \mathcal{R}_0$, and the micelle concentration, $c - \text{cmc} \approx c$ (as explained above), are related to the inverse osmotic compressibility, $\partial \Pi / \partial c$, by¹⁸

$$\frac{K_0 c}{\Delta \mathcal{R}_0} = \frac{1}{kT} \left(\frac{\partial \Pi}{\partial c} \right) \quad (7)$$

where k is the Boltzmann constant and T is the absolute temperature. In general, the structure factor, $S(0)$, is also related to the inverse osmotic compressibility by¹⁹

$$\frac{1}{S(0)} = \frac{M}{kT} \left(\frac{\partial \Pi}{\partial c} \right) \quad (8)$$

Combining eqs 2, 7, and 8 yields the following general central relationship used in analyzing static light scattering data:

$$\frac{K_0 c}{\Delta \mathcal{R}_0} = \frac{1}{M S(0)} = \frac{1}{M_{\text{app}}} \quad (9)$$

If there are no intermicellar interactions, the structure factor $S(0) = 1$. If the structure factor is not accounted for explicitly, then the weight-average micelle molecular weight, M , is replaced by an apparent weight-average molecular weight, M_{app} , that is, $M S(0) = M_{\text{app}}$.

Note that in eq 9 both the Rayleigh ratio and the structure factor are evaluated at a scattering vector value of $Q = 0$. However, in our systems, $\Delta \mathcal{R}_\theta$ does not exhibit a strong angular dependence, and we can replace $\Delta \mathcal{R}_\theta$ in eq 9 with $\Delta \mathcal{R}_{\theta=90}$. As mentioned earlier, in the case of polydisperse micelles, M denotes the weight-average molecular weight, but for brevity, we will refer to it hereafter as the molecular weight or the average molecular weight.

The use of static light scattering to probe mixed micellar solutions poses interesting experimental challenges,³⁷ because at a given solution composition, both the composition and the size of the mixed micelle can change with surfactant concentration. Our approach involves applying eq 9 at every surfactant concentration and solution composition and obtaining M by calculating the structure factor, $S(0)$. Rigorously, for spherically symmetric monodisperse particles, $S(0)$ is related to the pair

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correlation function, $g(r)$, according to^{38,39}

$$S(0) = 1 + 4\pi\rho \int_0^\infty r^2 [g(r) - 1] dr \quad (10)$$

where ρ is the number density of scattering particles, or mixed micelles in the present case, and r is the distance from the center of the micelle. Note that because eq 10 assumes spherically symmetric particles, its application to nonspherical micelles requires replacing the micelle by an effective sphere of the same volume. This is a reasonable approximation for the mixed micelles considered here, because their aggregation numbers are relatively small. Note also that because eq 10 assumes monodisperse particles, if the micelles are polydisperse, $S(0)$ represents the structure factor for a monodisperse solution of average-sized micelles.

If $g(r)$ is known, then $S(0)$ can be calculated according to eq 10. The pair correlation function depends on the interaction potential between the micelles, $V(r)$. Several approximations have been developed to relate $g(r)$ to $V(r)$, including, in order of increasing complexity, the dilute gas or random phase approximation (RPA),^{20,39} the mean spherical approximation (MSA),^{40,41} and integral equations, such as the hypernetted chain (HNC) equation.^{38,42} Here, we use the dilute gas approximation to relate $g(r)$ to $V(r)$, because it yields the same results as the HNC formalism³⁸ and it is computationally simpler.

According to the dilute gas approximation, $g(r)$ is related to $V(r)$ for an effective sphere of radius R by³⁸

$$g(r) = \begin{cases} 0 & \text{for } r \leq R \\ \exp(-V(r)/kT) & \text{for } r > R \end{cases} \quad (11)$$

The fact that for $r \leq R$, $g(r) = 0$ in eq 11 translates into an excluded volume interaction potential. That is, if the micelles approach so that they touch each other, then the interaction potential becomes $V(r) = \infty$, resulting in $g(r) = 0$.

To calculate the pair correlation function, the interaction potential, $V(r)$, must be chosen to reflect the intermicellar interactions. Due to the presence of ionic surfactants in the mixed micelles, we expect repulsive electrostatic intermicellar interactions. As mentioned earlier, we neglect attractive intermicellar interactions because both the surfactant concentration and the temperature are low.^{26,28–30} Exact expressions for electrostatic intermicellar interactions exist only for spherical micelles. Therefore, as mentioned earlier, we approximate the micelles formed by the SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixtures as effective spheres of radius R , and we have utilized the repulsive part of the commonly used DLVO potential for $\kappa R > 1$, given by^{31,43}

$$V(r) = (\epsilon_w R \psi_0^2 / 2) \ln[1 + \exp(-\kappa r)] \quad (12)$$

with

$$\psi_0 = (2kT/e) \sinh^{-1} \left[\frac{e^2 z_m}{2R^2 \kappa \epsilon_w kT} \right] \quad (13)$$

where z_m is the effective number of charges on the micelle, $\epsilon_w = 4\pi\eta_w \epsilon_0$, with η_w the dielectric constant of water and ϵ_0 the permittivity of vacuum, and κ is the inverse Debye length, given by

$$\kappa = (8\pi C_0 e^2 z^2 / \epsilon_w kT)^{1/2} \quad (14)$$

It is appropriate to use eqs. 12 and 13 to describe the intermicellar interaction potential in our solutions, because they apply for $\kappa R > 1$, and in our surfactant solutions, $\kappa R > 2.5$. It is interesting to note that because the potential in eq 12 applies at relatively high ionic strengths (where $\kappa \gg 1$), it is more sensitive to the micelle size than to its charge, which is partially screened by the added salt.

Treating all the mixed micelles as effective spheres introduces some error into our calculations of the interactions, but the repulsive interactions are relatively weak due to the presence of NaCl (at a concentration of 0.1 M) in all our solutions. The structure factor, $S(0)$, represents the ratio of the actual intensity of scattered light to the intensity in the absence of interactions. In our solutions, $0.8 < S(0) < 1.0$, indicating that accounting for the interactions affects the results by 20% at most. Therefore, we believe that the error introduced by treating the mixed micelles as effective spheres is not very large. As another measure of this approximation, we can estimate the distance between the centers of the mixed micelles in the solution. Depending on the solution composition and surfactant concentration, this distance can range from approximately 200 to 300 Å, which is at least five times the radius of the effective spheres. At this distance, the micelles are not likely to sense elongated shapes. Nevertheless, accounting for the intermicellar interactions is important, because otherwise the apparent mixed micelle aggregation numbers display physically unreasonable trends in micelle size, such as a decrease in aggregation number with increasing surfactant concentration.

To calculate $S(0)$ according to eq 10, we calculate $g(r)$ given in eq 11, based on $V(r)$ given in eq 12. The potential in eq 12 depends on two unknowns: the radius of the particle, R , and its charge, z_m . Our goal is to determine N , the average mixed micelle aggregation number, and both R and z_m can be related to N . The radius of a spherical micelle can be related to its aggregation number by

$$R = \left(\frac{NV_s}{4\pi/3} \right)^{1/3} \quad (15)$$

where V_s is the average volume of a surfactant molecule, given by $V_s = \alpha V_s^A + (1 - \alpha) V_s^B$, where V_s^A and V_s^B are the volumes of surfactants A and B, respectively, and α is the mixed micelle composition. The surfactant volumes were calculated based on the surfactant molecular structures and are listed in Table 2 for each of the three surfactants considered. Note that in analyzing the SLS measurements, we have used the bare, unhydrated volumes of the surfactants, assuming that light scatters only from the surfactant itself and not from any hydrated water associated with the ethylene oxide groups.^{26,28}

In eq 13, the charge of the mixed micelle, z_m , is the effective charge of the micelle or the charge that would be experienced by another micelle in the solution. Small angle neutron scattering (SANS) measurements on mixed micelles have shown^{44,45} that for low ionic micelle com-

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Table 2. Surfactant Volume (V_s), Distance from the Micellar Core/Water Interface to the Surface of Charge (d_{ch}), and Head Cross-Sectional Area (a_h) for $C_{12}E_6$, SDS, and SDE₆S

surfactant	V_s (Å ³)	d_{ch} (Å)	a_h (Å ²)
$C_{12}E_6$	731.2		41.7
SDS	442.2	3.7	25.0
SDE ₆ S, globular	823.2	12.7	41.7
SDE ₆ S, extended	823.2	26.0	25.0

positions ($\alpha < 0.3$), there is very little counterion binding, because the nonionic heads shield the charged heads from each other. In that case, the effective charge of an ionic/nonionic mixed micelle is the same as its bare charge, which is determined by the micelle composition, that is, $z_m = \alpha N$. We have assumed that this relationship applies for $\alpha \leq 0.4$, the conditions at which we have performed all our measurements. As explained earlier, the interaction potential (eqs 12 and 13) is not very sensitive to the value of z_m , because it applies for a relatively high salt concentration, which partially screens the charges on the micelle. Under these conditions, the approximation of $z_m = \alpha N$ for $\alpha \leq 0.4$ is reasonable.

The surfactant concentrations at which we have measured the properties of the SDS/ $C_{12}E_6$ and SDE₆S/ $C_{12}E_6$ mixed micelles are much higher than the cmc's of these surfactant mixtures, and therefore, we can safely assume that the micelle composition, α , is the same as the solution composition, such that $\alpha \approx \alpha_{soln}$.^{2,14,35} The effective charge can then be calculated by $z_m = \alpha_{soln} N$. Using this relation together with eq 15 in eqs 12 and 13 allows us to express $V(r)$, and consequently $S(0)$, as a function of a single unknown, the average mixed micelle aggregation number, N .

Returning to eq 9, we can recast it as a function of the average mixed micelle aggregation number, N , such that

$$\frac{K_0 c}{\Delta \mathcal{R}_0} = \frac{1}{NM_w S(0)} \quad (16)$$

where M_w is the average molecular weight of a surfactant molecule such that

$$M_w = \alpha M_w^A + (1 - \alpha) M_w^B \quad (17)$$

with M_w^A and M_w^B the molecular weights of surfactants A and B, respectively. The average mixed micelle molecular weight is given by $M = NM_w$. The left-hand side of eq 16 is measured, M_w is known since $\alpha \approx \alpha_{soln}$, and $S(0)$ is a function of N . Using eqs 10–15, N is the only unknown, and it can be determined numerically at each total surfactant concentration and solution composition.

2. Micelle Hydrodynamic Radii. The diffusion coefficient measured by QLS reflects the collective diffusion of the micelles or the diffusion of the micelles as affected by the intermicellar interactions. As in SLS, if the size of the micelles does not change with surfactant concentration, the actual diffusion coefficient can be deduced by extrapolating the collective diffusion coefficient to the cmc,^{26,31,33} where intermicellar interactions are negligible. In general, the actual diffusion coefficient, D_0 , is related to the measured collective diffusion coef-

ficient, D_c , by³⁸

$$D_0 = D_c \left[\frac{S(0)}{1 + H(0)} \right] \quad (18)$$

where $H(0)$ is a factor reflecting hydrodynamic interactions³⁸ and $S(0)$ is the structure factor given by eq 10 and calculated as in section II.D.1 above. As explained above in the case of $S(0)$, the hydrodynamic factor $H(0)$ is calculated in the limit of $Q \rightarrow 0$, because the micelles are small enough that the scattered light does not exhibit a dependence on scattering angle.

The hydrodynamic interaction factor, $H(0)$, can be calculated at the level of the Oseen tensor according to³⁸

$$H(0) = 1 + 4\pi R \rho \int_0^\infty r [g(r) - 1] dr \quad (19)$$

Equation 18 was used to obtain D_0 for each value of D_c , measured as described in section II.C.3. Other methods of calculating $H(0)$ ^{31,32,38} gave the same results. The value of $S(0)$ used in eq 18 is the same as that calculated from the SLS analysis (see section II.D.1) for the same sample. $H(0)$ was calculated according to eq 19, using the same pair correlation function, $g(r)$, as was used in calculating $S(0)$. Accordingly, the diffusion coefficient was corrected for intermicellar interactions based on the same pair correlation function and the same structure factor as in the SLS analysis. The actual average hydrodynamic radius of the mixed micelles was determined from the diffusion coefficient, D_0 , by using the Stokes–Einstein relation,²² such that

$$R_h = \frac{kT}{6\pi\eta_0 D_0} \quad (20)$$

where η_0 is the viscosity of the aqueous salt solution in the absence of micelles.

3. Micelle Shape and Hydration. The SLS measurements yield the weight-average mixed micelle aggregation number, N , and the QLS measurements yield the average mixed micelle hydrodynamic radius, R_h , at each surfactant concentration and solution composition. The mixed micelle shape is then determined by combining N and R_h . As stated earlier, the assumption of effective spheres for the purpose of calculating the structure factor and determining N is not expected to significantly affect N , because the electrostatic intermicellar interactions are relatively weak. To verify this point, we determined the mixed micelle shape and hydration using aggregation numbers which had *not* been corrected for intermicellar interactions and obtained very similar results. In micelles that grow significantly and exhibit angular dependence in SLS measurements, the micelle shape has been determined^{23,46} by comparing the average radius of gyration, R_g , with the average R_h . In the present case, since the mixed micelles remained relatively small and we could not determine R_g , we followed an alternative approach, which involves considering the volume of the micelle, V_{mic} , and the R_h of that micelle.

Experimentally, the volume of a micelle can be determined according to^{26,28}

$$V_{mic} = N(V_s + V_h) \quad (21)$$

where V_s is the bare volume of the surfactant molecule

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Table 3. Volume (V), Hydrodynamic Radius (R_h), and Shape Factor (ν) for Prolate and Oblate Ellipsoids of Minor Radius a and Major Radius b

	prolate ellipsoid	oblate ellipsoid
V	$(4/3)\pi a^2 b$	$(4/3)\pi a b^2$
R_h	$\frac{b(1 - (a/b)^2)^{1/2}}{\ln\left[\frac{1 + (1 - (a/b)^2)^{1/2}}{a/b}\right]}$	$\frac{a((b/a)^2 - 1)^{1/2}}{\arctan(((b/a)^2 - 1)^{1/2})}$
ν	$\frac{24}{15} + \frac{(b/a)^2}{15} \left[\frac{1}{\ln(2b/a) - 1.5} + \frac{3}{\ln(2b/a) - 0.5} \right]$	$\frac{16(b/a)}{15 \arctan(b/a)}$

and V_h is the volume of hydrated water per surfactant molecule. The volume of the micelle must include the hydrated water, because the hydrodynamic radius measured by QLS corresponds to the hydrated micelle.

The shape of mixed micelles of a given composition was determined by assuming a constant value of V_h for each surfactant mixture, and then plotting V_{mic} as a function of R_h for mixed micelles at different surfactant concentrations. The volume of an individual water molecule was taken as 30 \AA^3 .⁴⁷ The experimental data were compared to mathematical relationships for the volumes and hydrodynamic radii of prolate and oblate ellipsoids¹⁸ (see Table 3 for these expressions), representing one-dimensional and two-dimensional growth, respectively. The fitting procedure described here is not sensitive enough to deduce the specific shape of the micelles, but the prolate and oblate ellipsoids are convenient models for distinguishing between growth in one and two dimensions, respectively. For both surfactant mixtures, the minor radius was 25 \AA , the sum of the length of the fully extended tail and the length of a coil of six EO groups. The major radius was varied so that V and R_h spanned the range of the experimental values. The micelle shape was determined by the best fit of the experimental data to one of the mathematical relationships between V and R_h . Other shapes, such as spheres and spherocylinders, are also possible. However, the aggregation numbers are large enough such that spheres are physically unreasonable, and we have found that for these micelles, spherocylinders are indistinguishable from prolate ellipsoids. Note that by varying V_h , the experimental data could be consistent with either the prolate ellipsoid or the oblate ellipsoid model, but only one of these shapes could be fit with a value of V_h that agrees with previously published^{28,48–51} experimental values of hydration in alkyl poly(ethylene oxide) surfactant micelles.

4. Viscosity Prediction. The viscosity measurements were performed as an independent check of the micelle size, shape, and hydration derived from the combined SLS and QLS measurements. The experimental viscosity, measured as described in section II.C.4, was compared to the predicted viscosity, using as inputs the micelle shape, size, and hydration determined as described in sections II.D.1–II.D.3. The relative viscosity η_r of a dilute micellar

solution is given by^{52,53}

$$\eta_r = 1 + \nu\phi + k_1(\nu\phi)^2 \quad (22)$$

where ν is the shape factor, k_1 is a constant, and ϕ is the hydrated volume fraction of the micelles. The shape factor accounts for the influence of micelle size on solution viscosity, and the quadratic term accounts for hydrodynamic interactions. For a dilute solution of rigid spheres, the quadratic term can be neglected, and $\nu = 2.5$ regardless of the size of the sphere, according to the Einstein equation.⁵² The shape factor has been calculated for prolate⁵² and oblate ellipsoids and is given in Table 3 for each of these shapes. The salt concentration was high enough (0.1 M) that electroviscous effects could be neglected.^{54,55}

To predict the viscosity, the shape factor was calculated based on the shape and dimensions of the micelles determined from the light scattering measurements. The volume fraction of micelles was calculated based on the hydrated volume of the micelles, with the hydration determined from the light scattering measurements.

III. Molecular-Thermodynamic Theory of Mixed Micellization

Our molecular-thermodynamic theory of mixed micellization has been previously described in detail.^{11,12,14} In this section, we briefly review the main components of the theory which will be useful in analyzing the predictions presented in section IV.

A. Free Energy of Mixed Micellization. The theory is based on calculating the size and composition distribution of the mixed micelles, which in turn depends on the free energy of forming a mixed micelle, g_{mic} . The free energy of mixed micellization is modeled as the sum of several free-energy contributions and an ideal entropy of mixing,^{11,12,14} as illustrated conceptually in Figure 1. *For each free-energy contribution, we have highlighted schematically only the relevant characteristics of the surfactant tails or the surfactant heads.*

The first three free-energy contributions involve only the surfactant tails. The transfer contribution, g_{tr} , accounts for transferring the surfactant tails of both surfactant types, drawn as long blue tails and shorter red tails, from the aqueous solution to the core of the mixed micelle, which is modeled at this stage as a binary oil mixture composed of the two tail types. The interfacial contribution, g_{int} , accounts for forming the interface, which is drawn in Figure 1 as a heavy dashed line, between the oil mixture representing the micellar core and the aqueous solution. The packing contribution, g_{pack} , accounts for anchoring one end of the tails of both surfactant types at the micellar core/water interface and packing the surfactant tails in the micellar core. If, as illustrated in Figure 1, the two surfactant types have tails of different lengths, they may pack better in the micellar core than tails that are all the same length and, thus, contribute to synergism in mixed micelle formation.

The last two free-energy contributions involve only the surfactant heads. The steric contribution, g_{st} , accounts for steric interactions between the surfactant heads, and this contribution can be responsible for synergism in mixed

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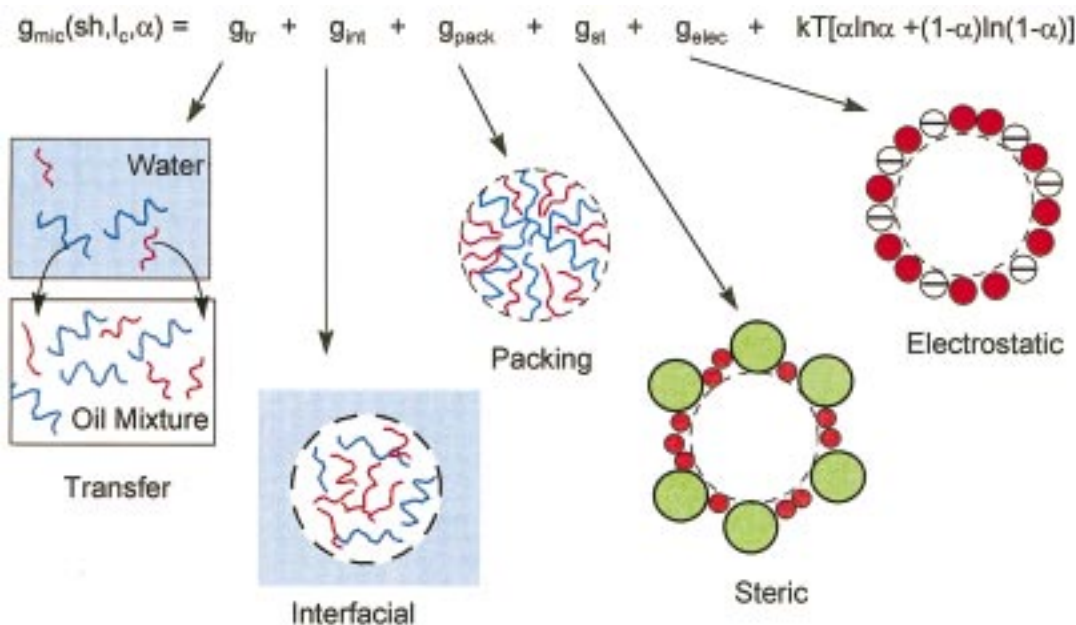


Figure 1. Schematic conceptual representation of the various free-energy contributions involved in the free energy of mixed micellization (see text for details). The schematic highlights only the surfactant characteristics relevant to each free-energy contribution. The free-energy contributions include transferring the tails of both surfactant types from the aqueous solution to the core of the mixed micelle, which is modeled as an oil mixture composed of the longer blue tails and the shorter red tails (g_{tr}); forming the interface, drawn as a heavy dashed line, between the oil mixture representing the micellar core and the aqueous solution (g_{int}); anchoring the surfactant tails at the micellar core/water interface and packing them in the micellar core (g_{pack}); accounting for steric interactions among the large green surfactant heads and the small red surfactant heads (g_{st}); and accounting for electrostatic interactions among the negatively charged surfactant heads and the red uncharged surfactant heads (g_{elec}).

micelle formation if the heads of the two surfactant types have different sizes, as illustrated by the large green heads and small red heads in Figure 1. The steric contribution depends only on the size of the surfactant heads. Finally, the electrostatic contribution, g_{elec} , accounts for electrostatic interactions between the surfactant heads. If, for example, negatively charged surfactant heads are mixed with uncharged surfactant heads (shown in red in Figure 1), the uncharged heads reduce the electrostatic repulsions between the charged heads and thus facilitate mixed micelle formation. The electrostatic contribution depends only on the electrostatic characteristics of the surfactant head, such as the valence of the charge and its location in the surfactant head.

The total free energy of mixed micellization is calculated as the sum of the free-energy contributions shown in Figure 1 and is then minimized with respect to the shape of the mixed micelle, its core radius, and its composition. In this study, we are predominantly concerned with the electrostatic and steric free-energy contributions to mixed micellization.

The electrostatic free energy, g_{elec} , is calculated as the reversible work of charging the mixed micelle to its final surface charge density. For ionic/nonionic mixed micelles, g_{elec} is given by¹⁴

$$g_{elec} = \int_0^1 [\psi_0(\lambda) q_f] d\lambda \quad (23)$$

where ψ_0 is the electrostatic surface potential, q_f is the final average charge per surfactant molecule, and λ is a charging parameter that varies from 0 to 1 as the mixed micelle evolves from being uncharged to being fully charged. The average charge per surfactant molecule depends on the micelle composition, α , such that $q_f = \alpha ze$, where z is the valence of the ionic surfactant and e is the electronic charge. The surface potential, ψ_0 , is an indirect function of the mixed micelle composition and is deter-

mined by solving an analytical approximation to the Poisson–Boltzmann equation. The procedure for calculating g_{elec} has been described in detail in ref 14. In general, the higher the ionic mixed micelle composition, the higher g_{elec} . Also, the higher the surface charge density, the higher g_{elec} . If the charged surfactant heads are closer together, as in cylindrical micelles, where the area per surfactant molecule is smaller, g_{elec} is higher. If the charged heads are farther apart, as in spherical micelles, g_{elec} is lower.

The steric free energy, g_{st} , accounts for steric interactions between the surfactant heads at the micellar interface. The surfactant heads are treated as a monolayer adsorbed at the micellar interface, and their interactions are described with a free energy derived from a two-dimensional equation of state given by¹⁴

$$g_{st} = -kT \left[\alpha \ln \left(1 - \frac{a_{hA}}{a} \right) + (1 - \alpha) \ln \left(1 - \frac{a_{hB}}{a} \right) \right] \quad (24)$$

where a_{hA} and a_{hB} are the head cross-sectional areas of surfactants A and B, respectively, and a is the area per surfactant molecule at the micellar core/water interface. As seen from eq 24, the larger the surfactant heads, the higher g_{st} . A smaller area per surfactant molecule, as in cylindrical micelles, leads to a higher g_{st} , while a larger area per surfactant molecule, as in spherical micelles, leads to a lower g_{st} .

B. Micelle Size. In the molecular-thermodynamic theory of mixed micellization,¹⁴ the size of the mixed micelles is determined by calculating the size and composition distribution. This distribution can be expressed as a function of two fundamental parameters which control the size of the mixed micelles. The first parameter, K , is defined as $K = e^{\Delta\mu/kT}$, with $\Delta\mu$ given by^{11,12}

$$\Delta\mu = n_{sph} [g_m^{sph} - g_m^{cyl}] + kT \quad (25)$$

where n_{sph} is the aggregation number of a spherical mixed micelle, and $g_{\text{m}}^{\text{sph}}$ and $g_{\text{m}}^{\text{cyl}}$ are modified free energies of mixed micellization of the optimum spherical and infinite cylindrical mixed micelles, respectively. The parameter $\Delta\mu$ determines whether the mixed micelles form spheres or cylinders. If $\Delta\mu < 0$, spheres are free-energetically more favorable, while if $\Delta\mu > 0$, cylinders are more favorable, and the mixed micelles grow. The second parameter, X_{cyl} , is defined as $X_{\text{cyl}} = e^{g_{\text{m}}^{\text{cyl}}/kT}$, with $g_{\text{m}}^{\text{cyl}}$ given by¹¹

$$g_{\text{m}}^{\text{cyl}}/kT = g_{\text{mic}}^{\text{cyl}}/kT - 1 - \alpha \ln \alpha_1 - (1 - \alpha) \ln(1 - \alpha_1) \quad (26)$$

where $g_{\text{mic}}^{\text{cyl}}$ is the free energy of mixed micellization of an infinite cylindrical mixed micelle, α is the mixed micelle composition, and α_1 is the monomer composition. Since $g_{\text{m}}^{\text{cyl}}$ is a measure of the free-energy cost of adding a surfactant molecule to the cylindrical portion of the mixed micelle, then X_{cyl} can be viewed as the cmc for forming an infinitely large cylindrical mixed micelle. The lower the value of $g_{\text{m}}^{\text{cyl}}$, the more favorable it is to add a surfactant molecule to the cylindrical portion of the mixed micelle, and the easier it is for the mixed micelle to grow. The parameters K and X_{cyl} are discussed more fully in refs 11, 12, and 18.

We have shown¹⁴ that for large n , the mixed micelle size and composition distribution is sharply peaked in composition at α^* , and consequently, it is reasonable to assume that each mixed micelle of aggregation number n has a single optimal composition, $\alpha^*(n)$. This approximation is discussed more fully in refs 11, 12, and 14. The mixed micelle size and composition distribution can then be written as¹¹

$$X_{n\alpha^*} = \frac{1}{K} \left(\frac{X_1}{X_{\text{cyl}}} \right)^n \quad (27)$$

where $X_{n\alpha^*}$ is the mole fraction of a mixed micelle of aggregation number n and composition α^* , X_1 is the mole fraction of monomers, and K and X_{cyl} are evaluated at α^* .

We are interested in the weight-average mixed micelle aggregation number as a measure of the micelle size, because this is the average aggregation number measured by static light scattering (N in section II.D.1). We have shown¹¹ that the weight-average aggregation number of a mixed micelle can be calculated from the second moment of the micelle size and composition distribution, such that

$$\langle n \rangle_{\text{w}} = \frac{\sum_{n>1} n^2 X_{n\alpha^*}}{\sum_{n>1} n X_{n\alpha^*}} \quad (28)$$

Note that the summation in eq 28 excludes the monomers. The theoretical aggregation numbers in section IV were predicted using eq 28. By substituting eq 27 in eq 28, we can identify the parameters that control the weight-average mixed micelle aggregation number. This substitution results in

$$\langle n \rangle_{\text{w}} = \frac{\frac{1}{K} \sum_{n>1} n^2 \left(\frac{X_1}{X_{\text{cyl}}} \right)^n}{\frac{1}{K} \sum_{n>1} n \left(\frac{X_1}{X_{\text{cyl}}} \right)^n} \quad (29)$$

Note that because K does not depend strongly on n , it can be removed from the summation, and since it is present in both the numerator and the denominator of eq 29, it

cancels out. Summing over n , we find that if the monomer concentration is approximately constant with composition, then $\langle n \rangle_{\text{w}}$ is largely determined by X_{cyl} and, consequently, by the free-energy contributions to forming an infinite cylindrical mixed micelle. Therefore, in analyzing the predicted values of $\langle n \rangle_{\text{w}}$, we can focus on examining only the contributions to $g_{\text{m}}^{\text{cyl}}$, which controls the value of X_{cyl} .

It is noteworthy that in this analysis, the factors controlling the mixed micelle aggregation number as a function of solution composition differ from those controlling the mixed micelle aggregation number as a function of the total surfactant concentration. In the limit of extensive micellar growth, it has been shown^{56,11,12} that the parameter K governs the change in $\langle n \rangle_{\text{w}}$ with total surfactant concentration, with K depending on both the cylindrical and spherical free-energy contributions to micellization. The analysis here differs in that experimentally the total surfactant concentration, X , is fixed. Then, if X_1 does not change significantly with the solution composition, α_{soln} , we can assume a constant value of X_1 . Although both X_1 and X_{cyl} may change with solution composition, X_{cyl} depends exponentially on $g_{\text{m}}^{\text{cyl}}$, and consequently, $\langle n \rangle_{\text{w}}$ reflects changes in $g_{\text{m}}^{\text{cyl}}$ much more strongly than it reflects changes in X_1 .

C. Molecular Parameters. The only inputs to the theory are the molecular structures of the surfactants and the solution conditions, including the temperature of the solution, the concentration and type of added salt, and the solution concentration and composition. The alkyl tails of the three surfactants studied are characterized by the number of carbons (12) in each tail. For the surfactant heads, the electrostatic free energy calculation requires that both the valence of the head and the distance from the micellar core/water interface to the location of the charge, d_{ch} , be specified. The steric free energy calculation depends on a_{h} , the cross-sectional area of the effective spherical surfactant head. More details on the estimation of all the relevant surfactant molecular parameters can be found in refs 57 and 58. The values of these molecular parameters are summarized in Table 2 for C_{12}E_6 , SDS, and SDE₆S, and are described below in more detail for each surfactant.

C₁₂E₆. Since C_{12}E_6 is nonionic, we only need to know a_{h} , the cross-sectional area of the head. Assuming a globular conformation for the ethylene oxide chain, the cross-sectional area can be calculated⁵⁶ based on the number of EO groups and their hydration, which depends on temperature. This approximate calculation results in $a_{\text{h}} = 42.3 \text{ \AA}^2$ at 25 °C.

SDS. The values of d_{ch} and a_{h} for the sulfate head of SDS can be calculated in a straightforward manner based on the bond lengths and bond angles of the sulfate group, resulting in $d_{\text{ch}} = 3.7 \text{ \AA}$ and $a_{\text{h}} = 25.0 \text{ \AA}^2$. Note that d_{ch} includes the first CH_2 group in the surfactant tail, to account for its polarity due to its proximity to the polar head.^{56,11–13}

SDE₆S. Describing the head of SDE₆S is less straightforward, because the conformation of the EO chain is determined by two competing effects. Unlike the EO chain of C_{12}E_6 , the EO chain of SDE₆S is capped by a sulfate ion. At one extreme, the EO chain could be fully extended, resulting in $d_{\text{ch}} = 26.0 \text{ \AA}$, corresponding to the length of six fully extended EO groups, and $a_{\text{h}} = 25.0 \text{ \AA}^2$, corresponding to the cross-sectional area of the sulfate group, which is the widest point of the head. This conformation would maximize the distance from the micellar core–water interface to the charge on the sulfate group, thus

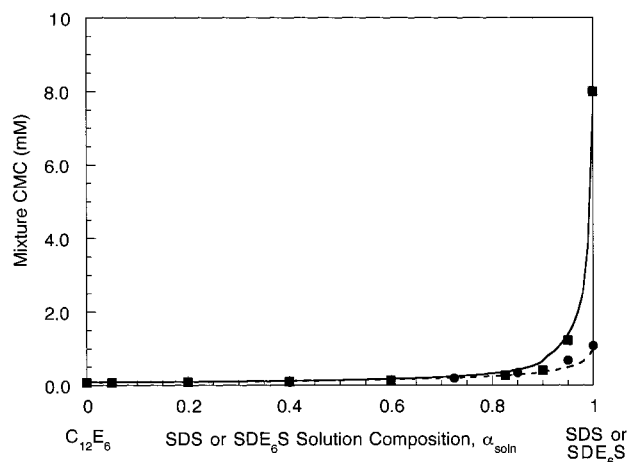


Figure 2. Mixture cmc as a function of ionic solution composition, α_{soln} , for aqueous SDS/ C_{12}E_6 (squares and solid line) and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (circles and dashed line) mixtures at 25 °C. The symbols denote experimental cmc values, with the error smaller than the size of the symbol, and the lines are theoretical predictions.

minimizing the surface charge density and the associated electrostatic free energy. However, an extended EO chain conformation is unfavorable from an entropic point of view, because the chain loses rotational and conformational degrees of freedom. At the other extreme, the EO chain could adopt the same globular conformation as in the nonionic C_{12}E_6 case ($d_{\text{ch}} = 12.7 \text{ \AA}$ and $a_{\text{h}} = 42.3 \text{ \AA}^2$, corresponding to the length and cross-sectional area calculated for the C_{12}E_6 head). This conformation would be favorable entropically, since it allows for more degrees of freedom, but it may be unfavorable electrostatically, since it would increase the surface charge density by bringing the charges closer to the micellar core/water interface.

It is likely that the molecular parameters of SDE_6S vary with the composition of the mixed micelle. Specifically, if the composition of SDE_6S is high, then the EO chain is likely to be more extended to minimize the electrostatic repulsions. If the composition of SDE_6S is low, the electrostatic free energy is less important and the conformational entropy of the EO chain may be increased by allowing the EO chain to adopt a more globular conformation.

In the predictions in section IV, we will set the molecular parameters of SDE_6S at either the extended or the globular EO chain conformations. For simplicity, we will consider only these two extremes, without varying d_{ch} or a_{h} with micelle composition. By comparing the experimental data to properties predicted with either the extended or the globular parameters, we will be able to infer the conformation of the EO chain in mixed micelles of different compositions.

IV. Experimental Results and Theoretical Predictions

A. Mixture cmc. Intramicellar interactions in surfactant mixtures are generally studied at the cmc, where their effect on mixed micelle formation can be measured. Figure 2 shows the experimentally measured mixture cmc as a function of the solution composition of ionic surfactant, α_{soln} , for the SDS/ C_{12}E_6 system (squares) and for the $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ system (circles). The solid and dashed lines are theoretical values of the mixture cmc's predicted using the molecular-thermodynamic theory described in section III. The predictions for the $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ system (dashed

line) at all solution compositions were generated using the molecular parameters for a fully extended EO chain.

Comparing the cmc's of the pure ionic surfactants in Figure 2 can provide some insight on the differences in structure between SDS and SDE_6S and on the conformation of the EO chain in SDE_6S . The cmc of SDS ($\approx 8 \text{ mM}$) is higher than that of SDE_6S ($\approx 1 \text{ mM}$). In SDS, the charged sulfate group is located close to the micellar core/water interface ($d_{\text{ch}} = 3.7 \text{ \AA}$), resulting in a high surface charge density. This high surface charge density, in turn, results in a high electrostatic free energy and, therefore, in a high cmc. In contrast, in SDE_6S , the charge is displaced from the micellar core/water interface by the six EO groups, resulting in a lower surface charge density, a lower electrostatic free energy, and a correspondingly lower cmc. The theoretical cmc prediction for pure SDE_6S agrees best with the experimental cmc value when the EO chain is assumed to be fully extended ($d_{\text{ch}} = 26.0 \text{ \AA}$). This is a logical conformation for a pure ionic micelle, where the drive to minimize the electrostatic repulsions between the surfactant heads is likely to dominate the conformational entropic loss associated with a fully extended EO chain.

Figure 2 shows that as soon as C_{12}E_6 is added to either SDS or SDE_6S , the experimental cmc values of the SDS/ C_{12}E_6 mixtures are similar to those of the $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ mixtures. Indeed, in the range $0 < \alpha_{\text{soln}} < 0.6$, the squares and circles denoting the experimental cmc values completely overlap. Even at an ionic solution composition of 0.95, where there is very little of the common nonionic surfactant, the mixture cmc's are similar. The predictions of the mixture cmc's for both mixtures agree well with the experimental cmc values over the entire composition range. Note that in predicting the cmc's in Figure 2, we have assumed that the monomer composition, α_1 , is equal to the solution composition, α_{soln} . At surfactant concentrations close to the cmc, this is a very good approximation.^{4,13}

The predicted mixture cmc's of the $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ mixtures were generated assuming a fully extended EO chain for SDE_6S at all solution compositions, to be consistent with the prediction for pure SDE_6S . However, we have found that except for pure SDE_6S , the predicted mixture cmc's are very similar regardless of whether an extended or a globular EO chain in SDE_6S is assumed. The cmc is probably not very sensitive to the conformation of the EO chain in SDE_6S because at $\alpha_{\text{soln}} < 1$, as shown in Figure 3, the mixed micelle is enriched in the nonionic surfactant, to minimize electrostatic repulsions between the charged SDE_6S heads. Since the micelle composition of SDE_6S is lower, the molecular parameters of SDE_6S are probably less important.

The experimentally observed cmc behavior of the SDS/ C_{12}E_6 and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ surfactant mixtures can be understood by analyzing the relevant g_{mic} contributions. In Figure 4, the predicted steric and electrostatic contributions to mixed micelle formation, g_{st} and g_{elec} , respectively, are plotted as a function of the solution composition, α_{soln} , for the SDS/ C_{12}E_6 (solid lines) and the $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (dashed lines) mixtures. The figure shows that g_{st} does not change significantly over the entire solution composition range, indicating that the steric contribution does not significantly influence mixed micelle formation at the cmc. However, g_{elec} exhibits a dramatic decrease from the pure ionic surfactant values, and therefore, it is the dominant contribution governing synergism at the cmc. The trend in g_{elec} with solution composition in Figure 4 parallels that of the mixture cmc with solution composition in Figure 2. The decrease in

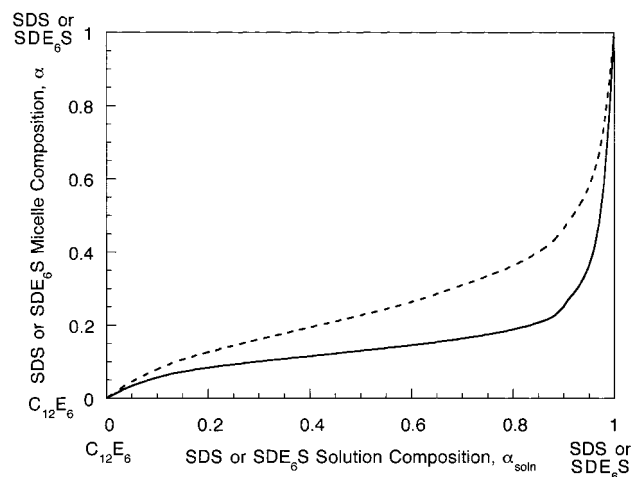


Figure 3. Predicted micelle composition, α , as a function of solution composition, α_{soln} , for SDS/ C_{12}E_6 (solid line) and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (dashed line) mixed micelles in aqueous solution at 25 °C at the mixture cmc.

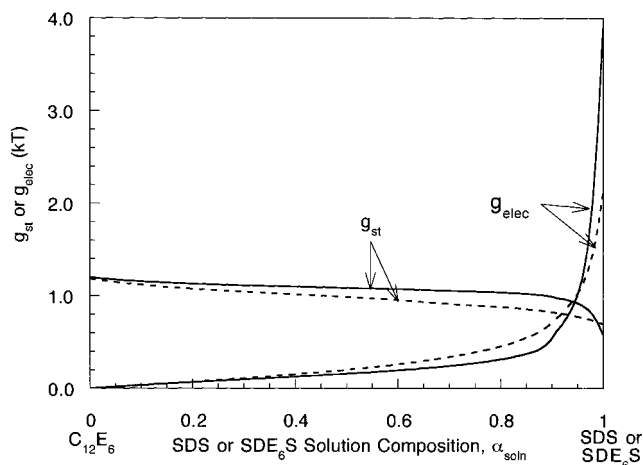


Figure 4. Predicted electrostatic (g_{elec}) and steric (g_{st}) free-energy contributions to mixed micelle formation as a function of solution composition, α_{soln} , for SDS/ C_{12}E_6 (solid lines) and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (dashed lines) mixed micelles in aqueous solution at 25 °C at the mixture cmc.

g_{elec} is due to the decrease of the electrostatic repulsions between the charged SDS or SDE_6S heads when C_{12}E_6 is added to the micelles, and g_{elec} decreases so suddenly because the micelle composition is different from the solution composition. As Figure 3 shows, the mixed micelles are highly enriched in the nonionic C_{12}E_6 in both mixtures, and g_{elec} is low at relatively high values of α_{soln} because the micelle composition of SDS or SDE_6S in the micelle is much lower than the solution composition. Figure 4 shows that the EO groups in SDE_6S do not affect the mixture cmc, because the steric contribution is not very important. As already stated, we have assumed a fully extended conformation for the SDE_6S head in the predictions shown in Figures 2 and 4; if we instead assume a globular conformation, the steric contribution is slightly larger, but it changes even less over the entire solution composition range.

B. Micelle Size. In addition to synergism in mixed micelle formation, we are also interested in studying the effect of interactions between the surfactants on the size of mixed micelles at surfactant concentrations higher than the cmc, so that the theoretical predictions can be tested at both of these conditions. At the cmc, the micelles are relatively small, and it is also difficult to determine their

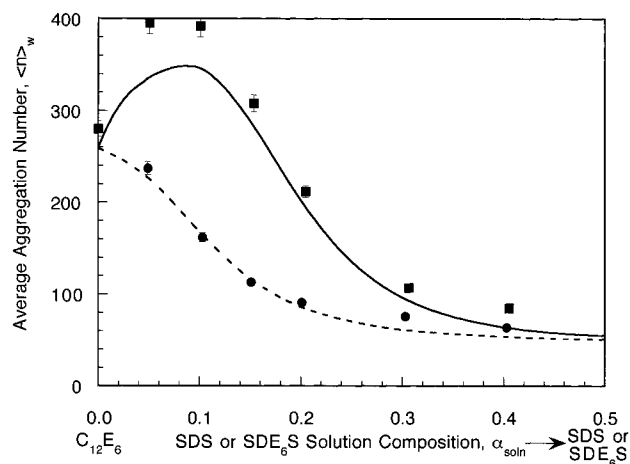


Figure 5. Weight-average micelle aggregation numbers, $\langle n \rangle_w$, as a function of ionic solution composition, α_{soln} , for SDS/ C_{12}E_6 (squares and solid line) and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (circles and dashed line) mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at a total surfactant concentration of 25 mM. The symbols denote experimental measurements, and the lines are theoretical predictions.

size experimentally. It has been shown^{12,28,34,59} that pure C_{12}E_6 micelles grow as the total surfactant concentration increases, and here, we examine the effect of the solution composition of SDS or SDE_6S on the growth of the SDS/ C_{12}E_6 and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ mixed micelles at 25 °C. To facilitate the light scattering measurement and analysis, we have performed these experiments at total surfactant concentrations between 10 and 50 mM in an aqueous 0.1 M NaCl solution. These surfactant concentrations are high enough (approximately 100 times the cmc) to easily measure the size and observe the growth of the mixed micelles. The concentration of added salt is high enough to somewhat screen the intermicellar electrostatic interactions but low enough to clearly observe synergism due to electrostatic intramicellar interactions between the surfactant heads.

We have measured the mixed micelle size for two sets of conditions. First, we fixed the total surfactant concentration at 25 mM and measured the micelle size as a function of the solution composition, α_{soln} . Next, we fixed α_{soln} at values of 0, 0.1, and 0.3 and measured the micelle size as a function of the total surfactant concentration. We have chosen the mixed micelle aggregation number as the primary indicator of micelle size, because this quantity can be directly predicted^{11,12,14} by the molecular-thermodynamic theory of mixed micellization described in section III.

1. Micelle Size as a Function of Solution Composition. Figure 5 shows the experimentally measured weight-average micelle aggregation numbers, $\langle n \rangle_w$, as a function of the solution composition of ionic surfactant for the SDS/ C_{12}E_6 (squares) and $\text{SDE}_6\text{S}/\text{C}_{12}\text{E}_6$ (circles) mixed micelles at 25 °C in 0.1 M NaCl at a total surfactant concentration of 25 mM. The lines are theoretically predicted values of the weight-average micelle aggregation numbers, $\langle n \rangle_w$, using the molecular-thermodynamic theory of mixed micellization described in section III. The apparent average micelle molecular weight, measured by static light scattering, was adjusted for intermicellar

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interactions as described in section II.D.1. At all solution compositions, we have assumed that the charge of the mixed micelle is determined by its composition, as discussed in section II.D.1. Note that in Figure 5, the solution composition is less than 0.5, because for $0.5 < \alpha_{\text{soln}} < 1.0$, the average micelle aggregation numbers show little change, approaching the values for pure SDS or pure SDE₆S. We have verified that the theoretically predicted weight-average micelle aggregation numbers of pure SDS and pure SDE₆S are also consistent with the experimental values.

To generate the predictions in Figure 5, the cross-sectional area of the pure C₁₂E₆ head was *fit* to approximately match the experimentally measured weight-average micelle aggregation number for pure C₁₂E₆ for these solution conditions, such that $a_h = 41.7 \text{ \AA}^2$ instead of 42.3 \AA^2 , as would be expected according to the theory without any fitting (see section III.C). Assuming that in the globular conformation, the size of the SDE₆S head is the same as that of the C₁₂E₆ head, the value of a_h for SDE₆S in the globular conformation was changed to 41.7 \AA^2 , to match that of C₁₂E₆. Note that the decrease of 0.6 \AA^2 in the cross-sectional area of the C₁₂E₆ head results in an increase in the weight-average aggregation number of C₁₂E₆ micelles from approximately 150 to 260. The size of the pure nonionic micelle is thus very sensitive to the value of a_h . Since a_h is estimated, we feel that this small adjustment to the pure surfactant molecular structure is reasonable, to more accurately study and understand the behavior of the surfactant mixtures. By use of the fitted value of a_h for C₁₂E₆ and SDE₆S, the predictions for the SDE₆S/C₁₂E₆ mixed micelles match the experimental measurements very well at all the other solution compositions, with an average difference between the predicted and experimental values of less than 1%. In the SDS/C₁₂E₆ mixtures, the experimental aggregation numbers are underpredicted by an average of 10%.

The trends of the aggregation number curves in Figure 5 can be understood based on the structures of the surfactants. In the case of SDS/C₁₂E₆, the aggregation number initially increases with solution composition, up to a maximum value at $\alpha_{\text{soln}} \approx 0.1$. At these low solution compositions, the electrostatic repulsions between the charged SDS heads are not yet important, but the introduction of the smaller SDS heads to the C₁₂E₆ micelle reduces the steric interactions between the larger C₁₂E₆ heads. The smaller steric free energy reduces the area required per surfactant head, allowing the mixed micelle to adopt a structure with lower curvature and resulting in the growth of the mixed micelle. At $\alpha_{\text{soln}} > 0.1$, the ionic micelle composition is high enough that the electrostatic repulsions between the charged SDS heads result in an increase in g_{elec} that dominates the decrease in g_{st} , and a subsequent increase in the area required per surfactant head. The mixed micelle consequently adopts a structure with a higher curvature, and the aggregation number decreases. The peak in aggregation number in the SDS/C₁₂E₆ mixture is thus due to an interplay between the steric and electrostatic free-energy contributions to mixed micellization. Note that the location of the peak is determined by the micelle composition. Over a very wide range of total surfactant concentrations, the micelle composition is the same as the solution composition. Therefore, at other surfactant concentrations, the size of the peak changes, because the aggregation number depends on the total surfactant concentration, but its location remains at $\alpha_{\text{soln}} \approx 0.1$.

In contrast, in the SDE₆S/C₁₂E₆ mixture, the average mixed micelle aggregation number in Figure 5 exhibits a

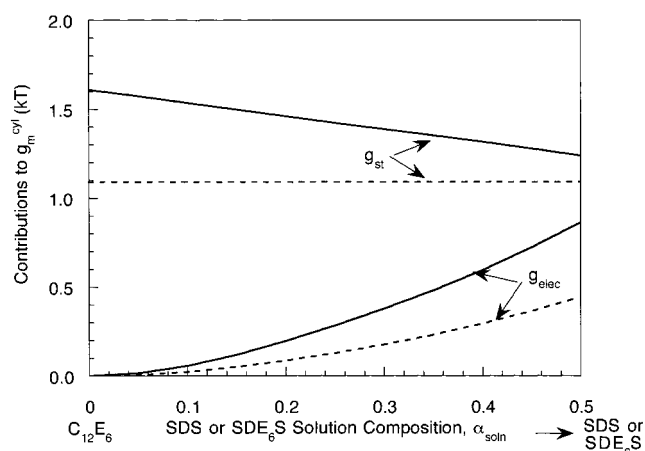


Figure 6. Predicted electrostatic (g_{elec}) and steric (g_{st}) free-energy contributions to the cylindrical modified free energy of mixed micellization ($g_{\text{m}}^{\text{cyl}}$) as a function of solution composition, α_{soln} , for SDS/C₁₂E₆ (solid line) and SDE₆S/C₁₂E₆ (dashed line) mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at a total surfactant concentration of 25 mM.

monotonic decrease. Because the SDE₆S heads are approximately the same size as the C₁₂E₆ heads, there is no reduction in steric free energy upon introducing SDE₆S surfactants to the pure C₁₂E₆ micelle. The decrease in the average mixed micelle aggregation number is due to the increase in electrostatic free energy as the ionic composition of the mixed micelle increases, and the mixed micelle prefers a smaller structure with a higher curvature.

More quantitatively, in Figure 6, we plot the predicted steric and electrostatic contributions to the free energy associated with forming a cylindrical mixed micelle as a function of solution composition, α_{soln} . As discussed in section III, the cylindrical free energy, $g_{\text{m}}^{\text{cyl}}$, determines the change in the weight-average mixed micelle aggregation number with solution composition. The lower $g_{\text{m}}^{\text{cyl}}$, the greater the propensity for the mixed micelle to grow. In the SDS/C₁₂E₆ mixed micelles, g_{st} decreases with solution composition, because the SDS head is smaller than the C₁₂E₆ head, but g_{elec} increases with solution composition, as the composition of the charged SDS head in the micelle increases. The sum of these contributions results in a minimum in $g_{\text{m}}^{\text{cyl}}$ at $\alpha_{\text{soln}} \approx 0.1$, which corresponds to the maximum in the aggregation number in Figure 5. In contrast, in the SDE₆S/C₁₂E₆ mixed micelles, g_{st} is approximately constant, because the heads of the two surfactants are approximately the same size. However, g_{elec} increases with solution composition, as the composition of the charged SDE₆S head in the mixed micelle increases. The sum of these two contributions results in a monotonic increase in $g_{\text{m}}^{\text{cyl}}$, which is responsible for the monotonic decrease in the aggregation number observed in Figure 5.

To achieve the agreement of the predicted average micelle aggregation numbers with the experimentally measured ones for the SDE₆S/C₁₂E₆ micelles in Figure 5, we have assumed a globular conformation for the EO chain in SDE₆S. The cross-sectional area of the head in this conformation is the same as that of the C₁₂E₆ head and differs from the extended EO chain conformation used in the cmc predictions shown in Figure 2. It is logical that over the relatively low ionic composition range examined in Figure 5 ($\alpha_{\text{soln}} \leq 0.5$), C₁₂E₆ will shield the charged heads enough that they do not need to be fully extended to maximize the distance between them and thus minimize the surface charge density. Although we can conjecture

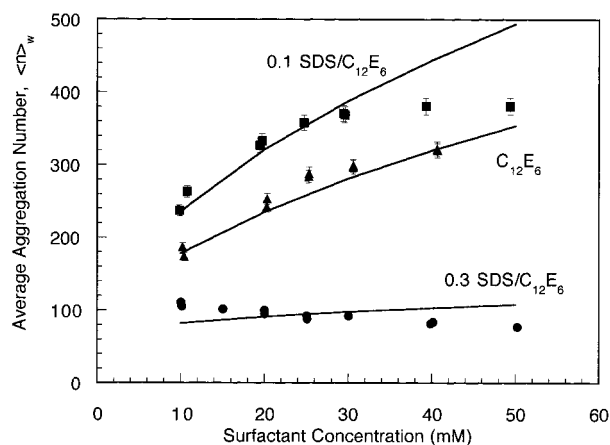


Figure 7. Weight-average micelle aggregation numbers, $\langle n \rangle_w$, as a function of surfactant concentration for SDS/C₁₂E₆ mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (squares), 0.3 (circles), and 0 (triangles, pure C₁₂E₆). The symbols denote experimental measurements, and the lines are theoretical predictions.

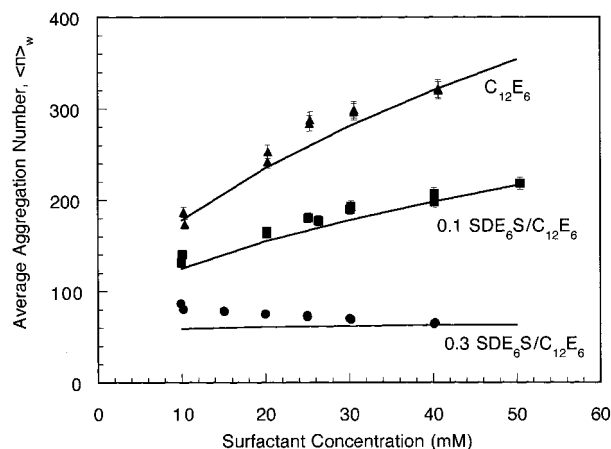


Figure 8. Weight-average micelle aggregation numbers, $\langle n \rangle_w$, as a function of surfactant concentration for SDE₆S/C₁₂E₆ mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (squares), 0.3 (circles), and 0 (triangles, pure C₁₂E₆). The symbols denote experimental measurements, and the lines are theoretical predictions.

that the EO chain conformation in the SDE₆S head changes from globular to extended as α_{soln} goes from 0 to 1, the predictions agree well with the experimental values over the range $\alpha_{\text{soln}} \leq 0.5$ even if we assume a constant globular conformation. The change in EO conformation from globular to extended may be gradual and may not influence the aggregation number significantly over this composition range.

2. Micelle Size as a Function of Surfactant Concentration. In addition to the micelle size as a function of solution composition at a single surfactant concentration (25 mM), we have also measured the micelle size at a given solution composition as a function of surfactant concentration. In Figures 7 and 8, the weight-average aggregation number, $\langle n \rangle_w$, of SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed micelles, respectively, at $\alpha_{\text{soln}} = 0.1$ (squares) and 0.3 (circles), is plotted as a function of surfactant concentration, together with the aggregation number of pure C₁₂E₆ micelles ($\alpha_{\text{soln}} = 0$, triangles). The symbols denote experimental measurements, and the lines are theoretical predictions. The experimental aggregation numbers reflect the intermicellar interactions as calculated in section II.D.1. The predictions were made using the same parameters used to generate the predictions in

Figure 5, and they agree reasonably well with the experimental values. The average difference between the predicted and experimental values varies between 3% and 15%, depending on the mixture and the solution composition.

In Figure 7, the SDS/C₁₂E₆ mixed micelles at $\alpha_{\text{soln}} = 0.1$ grow more than the pure C₁₂E₆ micelles, with a more rapid increase in aggregation number as the surfactant concentration is increased. However, at $\alpha_{\text{soln}} = 0.3$, the aggregation number of the SDS/C₁₂E₆ mixed micelles is approximately constant. These trends are consistent with the measurements in Figure 5. At the low ionic composition ($\alpha_{\text{soln}} = 0.1$), the smaller SDS heads reduce the steric repulsions, resulting in a smaller area per surfactant molecule and an increase in aggregation number. In contrast, at $\alpha_{\text{soln}} = 0.3$, the electrostatic repulsions between the charged SDS heads are strong enough to prevent micelle growth, as they typically do in the case of pure ionic surfactants. The nonmonotonic behavior of the micelle aggregation number with composition in Figure 7 thus corresponds to the maximum in aggregation number in Figure 5. The overprediction of the aggregation numbers at $\alpha_{\text{soln}} = 0.1$ at the higher surfactant concentrations may be due to the repulsive intermicellar interactions. At higher surfactant concentrations, these repulsive interactions are stronger, and the assumed interaction potential, which applies for dilute solutions, may be slightly too weak.

In Figure 8, the SDE₆S/C₁₂E₆ mixed micelles grow *less* than the pure C₁₂E₆ micelles at both solution compositions. As in Figure 5, there is no reduction in the steric free energy when SDE₆S is introduced into the C₁₂E₆ micelle, because the size of the SDE₆S head is similar to the size of the C₁₂E₆ head. The increase in electrostatic free energy reduces the growth of the mixed micelle in comparison to that of the C₁₂E₆ micelles. As in Figure 7, at $\alpha_{\text{soln}} = 0.3$, the ionic composition of the mixed micelle is high enough to prevent micelle growth. In the predictions of Figure 8, as in those of Figure 5, we have assumed a globular conformation for the EO chain in SDE₆S.

Our findings clearly show that in contrast to micelle formation at the cmc, at the higher surfactant concentrations, the effect of the EO groups in SDE₆S is very noticeable and the steric contribution is important. If the SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixtures were only compared at the cmc, these differences could be easily overlooked.

C. Micelle Shape and Hydration. To determine the shape into which the mixed micelles grow at $\alpha_{\text{soln}} = 0.1$, we have combined the static light scattering measurements in Figures 7 and 8 with dynamic light scattering measurements for the same solutions. As described in section II.D.3, the micelle shape can be determined by examining the relationship between the micelle volume and its hydrodynamic radius. We consider micelle growth into two common shapes: one-dimensional growth, into a prolate ellipsoid shape, and two-dimensional growth, into an oblate ellipsoid shape. As explained earlier, we have found that spherocylinders are indistinguishable from prolate ellipsoids and that the aggregation numbers are large enough such that spheres are physically unreasonable.

In Figures 9 and 10, the average volumes of the mixed micelles, calculated by eq 21, are plotted as a function of their average hydrodynamic radii, measured as described in section II.D.2, for SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed micelles, respectively. In both cases, the ionic solution composition is $\alpha_{\text{soln}} = 0.1$ and the total surfactant concentration was varied from 10 to 50 mM, as in the measurements reported in Figures 7 and 8. The symbols

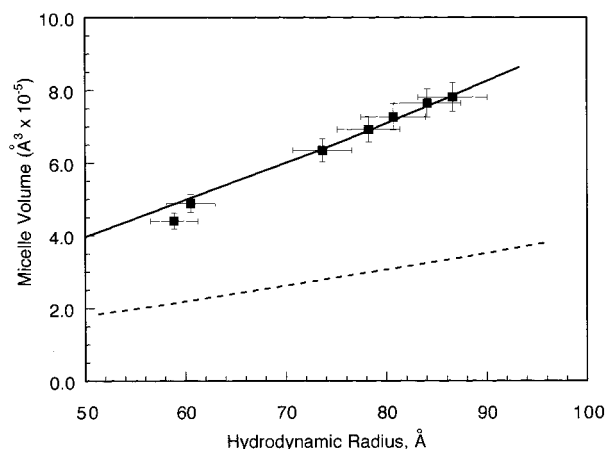


Figure 9. Experimental average micelle volume as a function of the experimental average micelle hydrodynamic radius for SDS/C₁₂E₆ mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (squares) with a hydration of 6.8 H₂O/EO group, together with mathematical relationships between volume and hydrodynamic radius for prolate (solid line) and oblate (dashed line) ellipsoids.

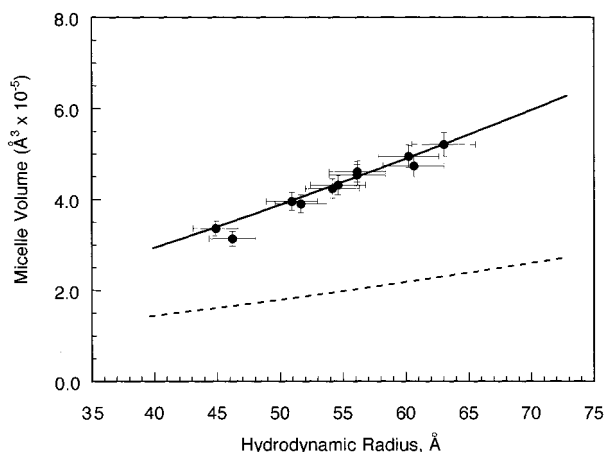


Figure 10. Experimental average micelle volume as a function of the experimental average micelle hydrodynamic radius for SDE₆S/C₁₂E₆ mixed micelles in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (circles) with a hydration of 9.0 H₂O/EO group, together with mathematical relationships between volume and hydrodynamic radius for prolate (solid line) and oblate (dashed line) ellipsoids.

denote experimental measurements of average hydrodynamic radii plotted with micelle volumes based on experimental measurements of micelle aggregation numbers. The lines are mathematical relationships for prolate (solid line) and oblate (dashed line) ellipsoids, with volumes and hydrodynamic radii calculated according to the expressions given in Table 3. The minor radius of the ellipsoid was assumed to be 25 Å, corresponding to the sum of the length of a fully extended C12 hydrocarbon tail and a globular head with six EO groups.

In both mixtures, the experimental data match the prolate ellipsoid model better than the oblate ellipsoid model. To achieve this match, a hydration of 6.8 H₂O/EO group was assumed for the SDS/C₁₂E₆ micelles, and a hydration of 9.0 H₂O/EO group was assumed for the SDE₆S/C₁₂E₆ micelles. A similar analysis was carried out for pure C₁₂E₆ micelles, resulting in a fit to the prolate ellipsoid model with a hydration of 7.5 H₂O/EO group. These values for the hydration are well within the range of experimentally measured hydration numbers for alkyl poly(ethylene oxide) surfactants.^{28,48–51} The hydration of the sulfate group in SDS and SDE₆S, taken to be 10 H₂O/

molecule,⁶⁰ was also taken into account. More specifically, for SDS/C₁₂E₆ mixed micelles, the volume of hydrated water per molecule, V_h , is given by

$$V_h(\text{SDS/C}_{12}\text{E}_6) = V_{\text{H}_2\text{O}}[10\alpha + 6(1 - \alpha)(\text{H}_2\text{O/EO})] \quad (30)$$

where $V_{\text{H}_2\text{O}} = 30 \text{ Å}^3$ is the volume of a water molecule, and H₂O/EO is the number of water molecules per EO group. For SDE₆S/C₁₂E₆ mixed micelles, V_h is given by

$$V_h(\text{SDE}_6\text{S/C}_{12}\text{E}_6) = V_{\text{H}_2\text{O}}[10\alpha + 6(\text{H}_2\text{O/EO})] \quad (31)$$

because the EO groups of both SDE₆S and C₁₂E₆ are hydrated. The volume of the mixed micelle could be adjusted depending on the value chosen for the hydration (H₂O/EO), and the experimental data could also fit the oblate ellipsoid model. However, to achieve this fit, the hydration would be less than 1 H₂O/EO in both mixtures, a value which is much lower than those reported in the literature.^{28,48–51}

At $\alpha_{\text{soln}} = 0.3$, the mixed micelles do not grow, and we cannot create plots similar to those in Figures 9 and 10. The hydration can nevertheless be determined by the difference in volume between the hydrated mixed micelle, based on R_h , and the bare volume, based on the aggregation number, that is,

$$V_h = \frac{V_{\text{mic}}}{N} - V_s \quad (32)$$

with V_{mic} corresponding to the volume of a hydrated sphere, because the mixed micelles exhibit little growth. The average hydration was found to be 9.5 H₂O/EO for the SDS/C₁₂E₆ mixed micelles, and 7.8 H₂O/EO for the SDE₆S/C₁₂E₆ mixed micelles, values that are similar to those of the mixed micelles at $\alpha_{\text{soln}} = 0.1$. The higher hydration of the SDS/C₁₂E₆ mixed micelles at $\alpha_{\text{soln}} = 0.3$ than at $\alpha_{\text{soln}} = 0.1$ is consistent with spin-echo modulation measurements⁵ which have shown that the hydration of SDS/C₁₂E₆ mixed micelles has a maximum at an equimolar micellar composition.

D. Micellar Solution Viscosity. As an independent check of the micelle size and shape determined by the combined SLS and QLS measurements, we also measured the relative viscosities of the mixed micellar solutions as a function of total surfactant concentration at $\alpha_{\text{soln}} = 0$ (pure C₁₂E₆), 0.1, and 0.3. All measurements were performed at 25 °C in aqueous 0.1 M NaCl solutions. The measured relative viscosities are plotted in Figure 11 for the SDS/C₁₂E₆ mixed micellar solutions and in Figure 12 for the SDE₆S/C₁₂E₆ mixed micellar solutions. The symbols represent experimental measurements, and the lines are drawn to guide the eye.

Qualitatively, the viscosity measurements agree very well with the light scattering measurements. In both mixtures, at $\alpha_{\text{soln}} = 0.3$, the relative viscosity increases linearly with total surfactant concentration, indicating that the mixed micelles are approximately spherical or that they do not grow enough for the viscosity measurement to detect the growth. This trend is consistent with the very small change in aggregation numbers reported for both mixtures in Figures 7 and 8 at $\alpha_{\text{soln}} = 0.3$. At $\alpha_{\text{soln}} = 0$ and 0.1, however, the viscosities are not linear with total surfactant concentration, indicating micelle growth,

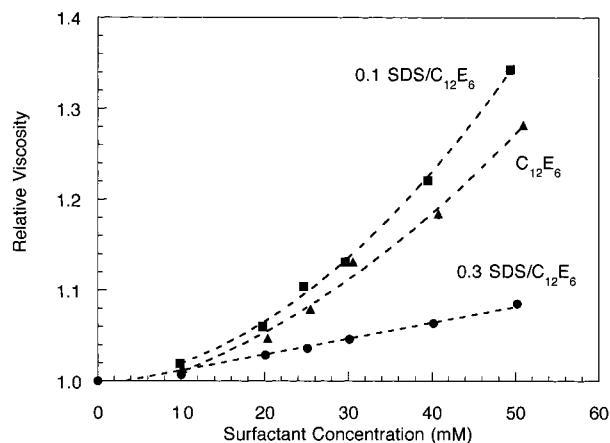


Figure 11. Relative viscosity as a function of surfactant concentration for SDS/C₁₂E₆ mixtures in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (squares), 0.3 (circles), and 0 (triangles, pure C₁₂E₆). The various lines are drawn to guide the eye, and the experimental error is smaller than the size of the symbols.

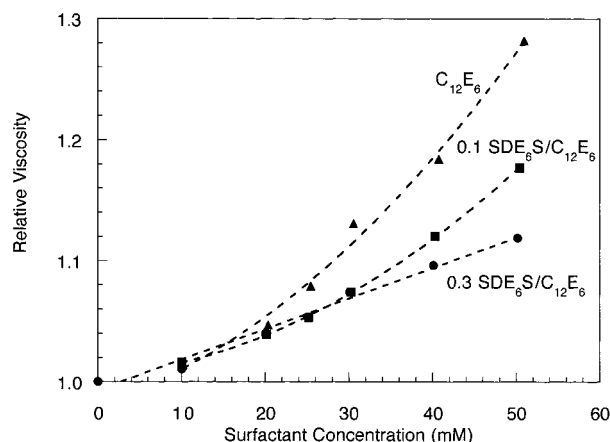


Figure 12. Relative viscosity as a function of surfactant concentration for SDE₆S/C₁₂E₆ mixtures in an aqueous 0.1 M NaCl solution at 25 °C at $\alpha_{\text{soln}} = 0.1$ (squares), 0.3 (circles), and 0 (triangles, pure C₁₂E₆) at 25 °C. The various lines are drawn to guide the eye, and the experimental error is smaller than the size of the symbols.

in accordance with eq 22. Higher viscosities correspond to larger micelles. At $\alpha_{\text{soln}} = 0.1$, the SDS/C₁₂E₆ mixed micelles grow more than the pure C₁₂E₆ micelles, as seen in Figure 11, and the SDE₆S/C₁₂E₆ mixed micelles grow less than the pure C₁₂E₆ micelles, as seen in Figure 12. This trend is again consistent with the aggregation numbers reported in Figures 7 and 8, which demonstrate that the SDS/C₁₂E₆ mixed micelles at $\alpha_{\text{soln}} = 0.1$ are larger than the C₁₂E₆ micelles, while the SDE₆S/C₁₂E₆ mixed micelles at this composition are smaller than the C₁₂E₆ micelles.

Quantitatively, however, if we predict the relative viscosity with eq 22 and the micelle shapes and dimensions deduced from the light scattering measurements, we overestimate the experimental relative viscosity by approximately 50%. The measured relative viscosities are very low for all the solutions ($\eta_r \leq 1.4$). A deviation of the plot of η_r as a function of ϕ from linearity indicates that the micelles grow, but the growth at such low values of η_r is very moderate. These micelles may be neither prolate nor oblate ellipsoids but may instead conform to some intermediate shape. To support this hypothesis, we extracted the hydration of the mixed micelles from the viscosity data at $\alpha_{\text{soln}} = 0.3$, where the micelles do not

grow, by fitting the experimental viscosity to⁵²

$$\eta_r = 1 + 2.5\phi \quad (33)$$

Equation 33 is the Einstein equation, which applies for spherical micelles. Given the measured η_r , the hydrated volume fraction, ϕ , can be determined, and related to the surfactant hydration. For both SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed micelles, we found a hydration of 4 H₂O/EO group, a value which is intermediate between that of prolate and oblate ellipsoids determined by light scattering for $\alpha_{\text{soln}} = 0.1$. The prolate ellipsoid shape may overestimate the hydration, but the oblate ellipsoid shape may underestimate it.

Viscosity measurements may also be less sensitive to micelle growth than light scattering measurements. For elongated micelles with axial ratios of less than approximately 4, the viscosity increase with total surfactant concentration is not very different from that due to spherical micelles.⁶¹ The axial ratios for the mixed micelles at $\alpha_{\text{soln}} = 0.1$ range from approximately 5 to 12, and if the viscosity is less sensitive to micelle growth at these ratios, it would increase less than that predicted.

V. Conclusions

We have studied the intramicellar and intermicellar interactions influencing both the formation and growth of SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed micelles through a combination of experimental measurements and theoretical predictions. The cmc's of both surfactant mixtures are very similar over most of the solution composition range, indicating that mixed micelle formation is governed primarily by electrostatic interactions between the surfactant heads, while steric interactions play a more minor role. The EO groups present in SDE₆S are not very important in determining mixed micelle formation, and SDE₆S behaves very similarly to SDS in mixtures with C₁₂E₆ at the cmc.

To study micelle growth at total surfactant concentrations above the cmc, we have used static and dynamic light scattering to measure the average aggregation numbers and the shape of the mixed micelles. In these measurements, the EO groups in SDE₆S are important, because the size of the mixed micelles is determined by an interplay of steric and electrostatic intramicellar interactions. At low ionic solution compositions, the SDS/C₁₂E₆ mixed micelles grow, because the addition of SDS, with a smaller head, reduces the steric repulsions between the larger C₁₂E₆ heads. The micelle size decreases at higher ionic solution compositions, as the electrostatic interactions between the SDS heads become important. The interplay of steric and electrostatic intramicellar interactions results in a maximum of the average SDS/C₁₂E₆ mixed micelle aggregation number with solution composition. In contrast, the average SDE₆S/C₁₂E₆ mixed micelle aggregation numbers decrease monotonically with increasing ionic solution composition, because there is no steric advantage to adding SDE₆S to the C₁₂E₆ micelles.

The measurement and prediction of the cmc of SDE₆S indicates that the EO chains adopt an extended conformation in the pure surfactant micelle. However, the measurement and prediction of the aggregation numbers of SDE₆S/C₁₂E₆ mixed micelles indicates that the EO chains adopt a more globular conformation in mixed micelles, when the solution composition is less than 0.5. It is likely that at solution compositions between 0.5 and 1, the EO chains gradually become more extended.

(61) Kohler, H.-H.; Strnad, J. *J. Phys. Chem.* **1990**, *94*, 7628.

By combining static and dynamic light scattering measurements of the micellar solutions at a given solution composition but at different total surfactant concentrations, we have demonstrated that both SDS/C₁₂E₆ and SDE₆S/C₁₂E₆ mixed micelles at $\alpha_{\text{soln}} = 0.1$ exhibit one-dimensional growth and that the hydration number of the surfactants in these micelles is 6.8 and 9.0 H₂O/EO group, respectively. The change in micelle size with concentration determined by the light scattering measurements overpredicts the change in size determined by viscosity measurements, perhaps because the mixed micelle shape is intermediate between prolate and oblate ellipsoids or because viscosity is less sensitive to micelle growth than light scattering. However, the qualitative trends observed from the two techniques agree well.

Most importantly, we have used the molecular-thermodynamic theory of mixed micellization to accurately predict the mixture cmc, as well as the aggregation numbers of the mixed micelles at various surfactant concentrations and solution compositions, fitting only the cross-sectional area of pure C₁₂E₆ to experimental measurements of the aggregation number. These measurements verify that the theory appears to be a useful tool

for analyzing the fundamental interactions in a surfactant mixture at the molecular level and for predicting solution properties of surfactant mixtures.

To more completely characterize these surfactant mixtures, the phase behavior could be studied by measuring the cloud-point curves at different ionic compositions. It has been shown that pure C₁₂E₆ aqueous solutions phase separate into micelle-rich and micelle-poor phases with increasing temperature and that the addition of ionic surfactants increases the temperature at which this phase separation occurs.⁷ It would be interesting to compare the effect of adding SDS and SDE₆S on the phase behavior of aqueous solutions of C₁₂E₆.

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