

Structure and composition of mixed micelles formed by nonionic block copolymers and ionic surfactants in water determined by small-angle neutron scattering with contrast variation

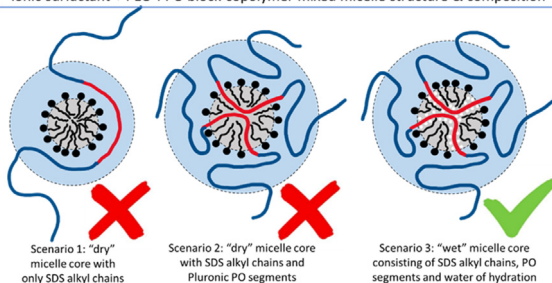
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GRAPHICAL ABSTRACT

Ionic surfactant + PEO-PPO block copolymer mixed micelle structure & composition



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ABSTRACT

Hypothesis: Complex fluids comprising polymers and surfactants exhibit interesting properties which depend on the overall composition and solvent quality. The ultimate determinants of the macroscopic properties are the nano-scale association domains. Hence it is important to ascertain the structure and composition of the domains, and how they respond to the overall composition.

Experiments: The structure and composition of mixed micelles formed in aqueous solution between poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers (Pluronics or Poloxamers) and the ionic surfactant sodium dodecylsulfate (SDS) are determined from an analysis of small-angle neutron scattering (SANS) intensity data obtained at different contrasts. Different polymers and concentrations have been probed.

Findings: The SDS + Pluronic mixed micelles include polymer and some water in the micelle core that is formed primarily by alkyl chains. This is different than what was previously reported, but is consistent with a variety of experimental observations. This is the first report on the structure of SDS + Pluronic P123 (EO₁₉PO₆₉EO₁₉) assemblies. The effects on the mixed micelle structure and composition of the surfactant concentration and the polymer hydrophobicity are discussed here in the context of interactions between the different components.

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1. Introduction

Block copolymers in selective solvent can assemble into micelles which are a manifestation of block segregation, and the

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building blocks of ordered block copolymer structures such as cubic, hexagonal, and lamellar.[1–7] The formation and structure of micelles reflect the balance between forces that favor self-assembly (e.g., segment-segment and solvent-solvent interactions) and those that oppose self-assembly (e.g., interface formation, chain stretching).[8–10] Enthalpy-driven micellization is typical in organic solvents, and entropy-driven micellization is common in aqueous solvents, pointing to the role of water organization around the water-insoluble block.[11,12] Block copolymer micelles have a core-shell structure, as ascertained from small-angle neutron scattering (SANS) and molecular dynamics (MD) simulations,[9,13–17] and the micelle size depends on the block copolymer molecular weight (MW).[13] Examples of block copolymers forming micelles in organic solvent include poly(isoprene)-*b*-poly(styrene) in *n*-decane, and poly(*tert*-butylmethacrylate)-*b*-poly[N-(4-vinylbenzyl)-*N,N*-diethylamine] in methanol.[18–20] In water, the best known and most studied block copolymers are members of a commercially available family called Pluronic of Poloxamers that have the block sequence poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO).[21–25] Applications of block copolymer micelles in, e.g., engine lubricants (in organic solvents), as drug carriers (in aqueous solvents), and in templated synthesis of nanomaterials,[26–31] highlight distinct advantages of block copolymer micelles compared to micelles assembled from low-MW surfactants: heat-induced break-up of micelles for lubricants, high loading capacity and colloidal stability for drug delivery, tunable size and robust organization (slow kinetics of disassembly) for materials synthesis. Block copolymer micelles are different from low-MW surfactant micelles in terms of their bigger size, higher chain flexibility, weaker degree of block segregation, and higher synthetic flexibility of the constituent amphiphiles.[13,17,32–34]

Mixed micelles, i.e., micelles incorporating more than one type of amphiphile, are unavoidable in the case of polydisperse block copolymers (having distribution of MW and of block length)[35–38] but are also formed intentionally by mixing different block copolymers in order to tune the solution properties and achieve desirable micelle structure/composition and function.[39,40] For example, mixed micelles consisting of the relatively hydrophilic Pluronic F127 PEO-PPO-PEO block copolymer and the relatively hydrophobic Pluronic P123 are used in pharmaceutical applications, whereby the hydrophobic P123 provides an environment conducive to the solubilization of water-insoluble drug molecules, while the long PEO chains of F127 confer stability in the aqueous solution and even “stealth” properties.[41] Low MW surfactants are commonly combined to form mixed micelles, as attested by the ingredients list of various consumer products.[42–44] Typical examples are mixtures of ionic and nonionic surfactants that achieve synergisms in lowering the critical micellization concentration (CMC) as well as other favorable properties.

Mixed micelles by block copolymers and low-MW surfactants are interesting in terms of their different modes of association and many potential applications.[45–54] The better studied are interactions between Pluronic PEO-PPO-PEO block copolymers and surfactants, in particular sodium dodecylsulfate (SDS).[46,49,55–65] Several techniques including isothermal titration calorimetry (ITC), light scattering, electromotive force (EMF), fluorescence, surface tension and SANS, concur that, with increasing SDS concentration, Pluronic-rich SDS/Pluronic F127 mixed micelles break down and form SDS-rich SDS/Pluronic F127 mixed micelles.[46,55–57,59,64] However, there is ambiguity regarding the structure and composition of the formed SDS/Pluronic assemblies. At lower SDS concentrations, where Pluronic-rich SDS/Pluronic mixed micelles form, a SANS study reported mixed micelles with 21 and 15 Pluronic F127 molecules at 1 mM and 2 mM SDS, respectively.[57] At the same temperature and concentrations, another SANS

study reported mixed micelles containing 54 and 42 Pluronic F127 molecules at 1 mM and 2 mM SDS, respectively.[64] At saturation, four to five molecules of SDS were found to bind to one Pluronic F127 molecule, for 1–3 wt% Pluronic F127 (estimated from the difference between SDS critical association and polymer saturation concentrations), and electric birefringence suggested that the SDS/Pluronic F127 assemblies are nonspherical.[63,64] This study further suggested (based on electric birefringence data) that Pluronic molecules have a stretched configuration and that SDS molecules adsorb in the PPO region.[63] Whereas another study reported the PEO-PPO-PEO molecules incorporated into the micelle shell.[57]

This study is motivated by the repercussions afforded from the mixing of two rather different types of amphiphilic molecules, Pluronic PEO-PPO-PEO block copolymer and SDS (nonionic and ionic, polyether and alkane, long and short, flexible and rather rigid), in modulating their self-assembly in water. The hydrophobic “attraction” is modulated by changing the type and length of the hydrophobic constituents, while the headgroup “repulsion” is modulated by changing the type and length of the hydrophilic group of the amphiphiles. Such information facilitates the design of formulated multi-component products.

We address here open questions on the structure and composition of the mixed micelles that are formed between nonionic amphiphilic polymer and ionic surfactant in aqueous solutions, and the effect on the micelle structure/composition of the polymer hydrophobicity and of the surfactant concentration. The nonionic amphiphilic polymers considered here are Pluronic F127 (EO₁₀₀-PO₆₅EO₁₀₀) and Pluronic P123 (EO₁₉PO₆₉EO₁₉).[66–68] The ionic surfactant is sodium dodecylsulfate (SDS), which is well studied and widely used in formulations.[69–71] The concentrations correspond to conditions where SDS is the majority component in the mixed micelles.[55] The structure and composition of the assemblies formed between Pluronic and SDS are determined from analysis of SANS data with contrast matching.

In the Results and Discussion section, we first present the mode of association of SDS with Pluronic block copolymer micelles in aqueous solution with increasing surfactant concentration. We then describe the SDS + Pluronic assembly structure and composition as obtained from analysis of SANS data obtained at two different contrasts, and discuss the effects of surfactant concentration and polymer hydrophobicity. We also compare the surfactant + polymer mixed micelle structure with that of polymer-free surfactant micelles in aqueous solution. The structure and composition of the SDS + Pluronic F127 mixed micelles that we conclude here on the basis of a thorough analysis of SANS data is different than that previously proposed in the literature, and is consistent with a variety of experimental observations other than SANS. This is the first report on the structure of SDS + Pluronic P123 assemblies.

2. Materials and methods

2.1. Materials

Information on the chemical compounds, their origin and purity, and sample preparation is presented in the [Supplementary Information](#) document.

The nonionic block copolymers Pluronic F127 and Pluronic P123 were selected on the basis of the same length PPO middle block and different length PEO blocks, which allows the study of polymer hydrophobicity effects. Pluronic P123 (EO₁₉PO₆₉EO₁₉) has shorter PEO blocks compared to Pluronic F127 (EO₁₀₀PO₆₅EO₁₀₀) and therefore Pluronic P123 is more hydrophobic. The ionic surfactant sodium dodecylsulfate (SDS) was selected since it is well studied and widely used in formulations. Aqueous mixtures of SDS and

Pluronic F127 or P123 have been previously studied.[46,56–60,62] The CMC values of Pluronic F127 and P123 are 0.89 wt% (0.71 mM) [72] and 0.12 wt% (0.21 mM)[11], respectively, in pure water at 22 °C, with corresponding average association numbers of 73 (5 wt% F127 at 25 °C)[73] and 81 (2.5 wt% P123 at 20 °C)[74], respectively. The concentrations of Pluronic F127 and Pluronic P123 considered in this study are 3 wt% and 0.5 wt%, respectively, both above the block copolymer CMC in water in the absence of added surfactant. SANS information on SDS + Pluronic assemblies formed at rather low, 1 and 2 mM, SDS concentrations (region II demarcated in our previous study[55]) has been previously published.[57] In this study we consider higher SDS concentrations, 16.6 mM and 110 mM for both Pluronics, in order to study SDS + Pluronic assembly structures that are formed in the composition regions III and IV of the polymer + surfactant system (refer to the Results and Discussion section).[55]

The scattering length density of the solvent D₂O matches that of deuterated SDS (d-SDS), hence the utilization of d-SDS can reveal structural information on the hydrogenous PEO-PPO-PEO block copolymers participating in SDS/Pluronic assemblies. The structural information of the entire SDS + Pluronic assemblies is obtained when hydrogenous SDS (h-SDS) is used.

2.2. Small-angle neutron scattering (SANS)

SANS has been widely used to determine the size and structure of PEO-PPO-PEO block copolymer micelles or low-MW surfactant micelles.[33,70,75] The large difference in the scattering lengths of hydrogen and deuterium provides a good contrast to reveal the structures formed by hydrogenous molecules in D₂O solvent. In the investigation of complex, multi-component systems, SANS performed at conditions of contrast matching provides a unique capability to obtain structural information on a certain sub-domain of an overall structure by matching the scattering contrast of other sub-domains to that of the solvent.

SANS measurements of aqueous polymer and surfactant solutions were carried out on the NG-7 and NG-B 30 m SANS instruments at the Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST), Gaithersburg, MD. Neutrons with 6 Å wavelength and wavelength spread ($\Delta\lambda/\lambda$) of 12 % were focused on samples kept in quartz cells of 1, 2 or 4 mm thickness. Sample-to-detector distances (SDD) of 2, 6.5 and 13 m, or 1.33, 4 and 13.17 m were used for each sample in order to span the wave vector (q) range $0.05 \text{ \AA}^{-1} < q < 0.5 \text{ \AA}^{-1}$. The measurement time was in the range 180–4200 s.

The scattering intensity originating from SDS-rich SDS + Pluronic assemblies was fitted using a combination of the core-shell ellipsoid form factor and Hayter rescaled mean spherical approximation (RMSA) structure factor with the correlation length model. The core-shell ellipsoid form factor and Hayter RMSA structure factor (details are provided in the subsequent text) have been widely used in the literature for describing ionic surfactant micelles.[70] Initial attempts to fit the scattering originating from SDS-rich SDS + Pluronic assemblies using only the core-shell ellipsoid form factor and Hayter RMSA structure factor, while successful at the high and intermediate q values, were not adequate at low- q values. The scattering intensity at low- q values may originate from a fraction of polymer molecules that cannot be described by the core-shell form factor. Hence, we incorporated to the overall scattering intensity the correlation length model. The correlation length model is a combination of Lorentzian and power law terms, and has been used to capture the scattering originating from nonionic polymers in aqueous solution.[70,76] The power law term describes Porod scattering from clusters, capturing the scattering behavior at low- q values. The Lorentzian term describes scattering

from polymer chains and captures the scattering behavior at high- q .[70,76] The overall scattering intensity $I(q)$ is then given by:

$$I(q) = scale_1 I(q)_1 + scale_2 I(q)_2 + B_{inc} \quad (1)$$

$I(q)_1$ is the intensity from the correlation length model which is calculated as:

$$I(q)_1 = \frac{A}{q^n} + \frac{C}{1 + (q\xi)^m} \quad (2)$$

The first term in Eq. (2) describes Porod scattering from clusters, with the power law exponent n capturing the scattering behavior at low q values. n reflects the mass fractal dimension of the clusters, and the scale factor A the scattering contribution of clusters. Clustering has been observed in many macromolecular systems, however, its origin has remained elusive.[76] Note that the low- q range examined in our SANS data captures only a small portion of the scattering originating from clusters,[76] hence, the cluster size cannot be properly determined from the present data.[76]

The second term in Eq. (2) is a Lorentzian function describing the scattering from polymer chains (exponent = m) which characterizes the polymer-solvent interactions and, therefore, the thermodynamics. ξ is a correlation length that describes the average distance between two polymer chain intersections in the case of semidilute polymer solution. For the Gaussian nature of Pluronic F127 or Pluronic P123 chains at that length scale, $m = 2$.[70] The scale factor C captures the solvation scattering of the polymer: a lower C value indicates more effective solvation.

$I(q)_2$ is the intensity from the core-shell ellipsoid form factor and the Hayter – Penfold structure factor with rescaled mean spherical approximation (RMSA). $I(q)_2$ is given by.[70]

$$I(q)_2 = \phi \cdot P(q) \cdot S(q) \quad (3)$$

$P(q)$ is the form factor representing the shape and structure of a micelle, while $S(q)$ is the structure factor representing the intermicelle interactions in the solution. ϕ is the volume fraction of the micelles which, in turn, depends on the overall surfactant concentration.

$P(q)$ is calculated using the following equations:

$$P(q) = \frac{1}{V} F^2(q, \alpha) + background \quad (4)$$

$$F(q, \alpha) = f(q, b, a, \alpha) + f(q, b + \delta, a + \delta \cdot \epsilon, \alpha) \quad (5)$$

where b is the core equatorial radius perpendicular to the rotational axis of the ellipsoid, a the polar core radius along the rotational axis of the ellipsoid, δ the thickness of the shell near the equator, and ϵ the ratio of the shell thickness at the pole to that at the equator. $\epsilon = 1$ for a fixed shell thickness.

$$F(q, R_e, R_p, \alpha) = \frac{3\Delta\rho V (\sin [qr(R_e, R_p, \alpha)] - \cos [qr(R_e, R_p, \alpha)])}{[qr(R_e, R_p, \alpha)]^3} \quad (6)$$

$$r(R_e, R_p, \alpha) = [R_e^2 \sin^2 \alpha + R_p^2 \cos^2 \alpha]^{1/2} \quad (7)$$

α is the angle between the axis of the ellipsoid and \vec{q} , $V = (4/3) \pi R_p R_e^2$ the volume of the ellipsoid, R_p the polar radius along the rotational axis of the ellipsoid, R_e the equatorial radius perpendicular to the rotational axis of the ellipsoid, and $\Delta\rho$ (contrast) the scattering length density difference, either $(\rho_{core} - \rho_{shell})$ or $(\rho_{shell} - \rho_{solvent})$. When the ratio of the micelle core radius (a) to the equatorial core radius (b) $\epsilon (=a/b) < 1$, the micelle core is oblate; when $\epsilon > 1$ it is prolate, while $\epsilon = 1$ denotes a spherical core.

The structure factor $S(q)$ is calculated using a Hayter–Penfold-type potential[77], with mean spherical approximation and rescaling corrections for low volume fractions, given the micelle volume fraction, charge on a micelle, and ionic strength of the solution.[70]

Table SI1 (available in [Supplementary Information](#)) lists the parameters (in the SASview software) that have been used here in fitting SANS data from SDS + Pluronic systems for the combination of the correlation length model with the core–shell ellipsoid form factor and Hayter MSA structure factor.

For the SDS and Pluronic concentrations (110 mM SDS + 3% Pluronic F127, 110 mM SDS + 0.5% Pluronic P123) where SDS-rich SDS + Pluronic assemblies coexist along with free SDS micelles in aqueous solution,[55] an additional core shell form factor and Hayter MSA structure factor term was considered in the overall scattering intensity equation $I(q)$:

$$I(q) = scale_1 I(q)_1 + scale_2 I(q)_2 + scale_3 I(q)_3 + B_{inc} \quad (8)$$

Here $I(q)_3$ describes scattering from SDS-only micelles, while $I(q)_2$ describes scattering from SDS-rich SDS + Pluronic assemblies. $I(q)_1$ is the intensity from the correlation length model. Both $I(q)_2$ and $I(q)_3$ intensities are captured by the core–shell ellipsoid form factor and the Hayter – Penfold structure factor with RMSA, described previously.

Various scenarios have been considered in this study for describing the composition of SDS-rich SDS + Pluronic mixed micelles (for details, please refer to [Supplementary Information](#)), including:

- (1) “dry” (no water present) micelle core consisting of only SDS alkyl chains, and micelle shell containing SDS headgroups, counterions, PO and/or EO segments from Pluronic block copolymer, and associated water of hydration;
- (2) dry micelle core consisting of SDS alkyl chains and Pluronic block copolymer PO segments, and micelle shell containing SDS headgroups, counterions, PO and/or EO segments from Pluronic block copolymer, and associated water of hydration;
- (3) “wet” micelle core consisting of SDS alkyl chains, Pluronic block copolymer PO segments and some associated water of hydration, and micelle shell containing SDS headgroups, counterions, PO and/or EO segments from Pluronic block copolymer, and associated water of hydration.

Among the three different structure/composition scenarios considered here, the one that describes best (refer to the [Supplementary Information](#)) the SDS-rich SDS + Pluronic assemblies is scenario number 3, which involves a micelle core that consists of SDS alkyl chains, Pluronic block copolymer PO segments and some associated water molecules; the micelle shell comprises SDS headgroups, counterions, PO and/or EO segments from Pluronic block copolymer and associated water of hydration; the remaining PO and/or EO segments are present in the bulk solution.

The expressions describing the micelle structure/composition for scenario 3 are presented in detail in SI. The surfactant association number (η) in SDS-rich SDS + Pluronic assemblies containing several SDS molecules and one (or two) Pluronic molecule is obtained from the mixed micelle core volume $V_{core} = \frac{4}{3}\pi ab^2 = \eta V_{t,SDS} + n_{PO,core} V_{PO} + N_{H,core} V_{D_2O}$, where $V_{t,SDS}$, V_{PO} , V_{D_2O} , are the volumes of SDS hydrocarbon chain, propylene oxide (PO) segment, and D_2O molecule, respectively. $n_{PO,core}$ is the number of PO segments in the micelle core, and $N_{H,core}$ the number of water molecules in the micelle core hydrating all the PO segments present there. The micelle shell volume V_{shell} (in \AA^3) is calculated from the volume contributions of the SDS headgroups, counterions, Pluronic block copolymer PO and/or EO segments in the shell, and associated water molecules, using $V_{shell} = \eta (V_{OSO_3^-} + (1 - \alpha)(V_{Na^+} + N_{H,Na^+} V_{D_2O}) + N_{H,OSO_3^-} V_{D_2O}) + n_{PO,shell} V_{PO} + n_{EO,shell} (V_{EO} + N_{H,shell} V_{D_2O})$, where $V_{OSO_3^-}$, V_{Na^+} , V_{EO} are the volumes of the SDS headgroup, Na^+ counterion, and EO segment, respectively. N_{H,Na^+} , N_{H,OSO_3^-} , $N_{H,shell}$ are the hydration numbers of the Na^+ counterion,

SDS headgroup, all the PO and EO segments present in the micelle shell, respectively. $n_{PO,shell}$ and $n_{EO,shell}$ are the number of PO and EO segments in the micelle shell, respectively. $\alpha = Z/\eta$ is the fractional charge on a micelle. Scattering length densities (SLD) of the micelle core ρ_{core} or micelle shell ρ_{shell} are calculated from the scattering length contributions of the groups/atoms present in the micelle core or shell, and the volumes of micelle core V_{core} or shell V_{shell} , respectively. The SLD of the solvent is $\rho_{solvent} = \rho_{D_2O} = 6.35 \times 10^{-6} \text{\AA}^{-2}$.

The key assumptions in analyzing the SANS data are that the micelle core minor radius (b) is equal to the extended length of the surfactant alkyl chain, the ratio of shell thickness at pole to that at the equator $\epsilon = 1$ (uniform shell thickness), and $N_{H,Na^+} = 6$ and $N_{H,OSO_3^-} = 8$ on the basis of the reported hydration numbers for Na^+ and OSO_3^- ions.[78] In fitting equation (1) to the scattering data, the number of micelle parameters that are really “free” is rather small: axial ratio of the micelle core, shell thickness, charge on the micelle, and volume fraction of micelles. Our confidence in the micelle structure/composition parameters reported in the article emanates from the fact that the same parameters fit two different scattering intensity data-sets (different scattering contrasts) for a given overall composition, and is further reinforced by the fact that the physical picture and trends that we report are consistent with a variety of previously published experimental results originating from very different techniques.

3. Results and discussion

The various interactions occurring between polymers and surfactants in solution contribute to the different structures of the assemblies formed.[70,79–84] When ionic surfactant is added to micellized nonionic PEO-PPO-PEO block copolymer in aqueous solution, Pluronic-rich surfactant/Pluronic assemblies (mixed micelles) initially form which, upon further increase in the ionic surfactant concentration and the ensuing electrostatic repulsions between the ionic surfactant headgroups, decrease in size and Pluronic association number, and transform into surfactant-rich surfactant/Pluronic assemblies. At even higher surfactant contents, these are accompanied by polymer-free surfactant micelles (Fig. 1). [55–57] The SDS and Pluronic concentrations probed here by SANS correspond to surfactant-rich surfactant/Pluronic assemblies.[55] Specifically, at 16.6 mM SDS + 3% Pluronic F127 and at 16.6 mM SDS + 0.5% Pluronic P123, SDS-rich SDS + Pluronic assemblies exist in the aqueous solution, while at 110 mM SDS + 3% Pluronic F127 and at 110 mM SDS + 0.5% Pluronic P123, SDS-rich SDS + Pluronic F127 assemblies coexist along with polymer-free SDS micelles in the solution.

The structure and composition of these surfactant-rich surfactant/Pluronic mixed micelles has remained elusive. A published SANS study on SDS-rich SDS + Pluronic F127 assemblies (formed at 100 mM hydrogenous SDS + 3% Pluronic F127 aqueous solution at 36.5 °C) has obtained structural parameters using the core–shell sphere form factor and Hayter RMSA structure factor.[57] This study assumed the micelle core to consist only of SDS alkyl chains (no polymer, no water), and the shell to consist of SDS headgroups with their corresponding hydration and a fraction of the Pluronic F127 chain (scenario 1 in [Supplementary Information](#)).[57] However, the hydration of Pluronic F127 chains in the micelle shell was not reported, and the scattering originating from the fraction of Pluronic F127 molecules present in solution (outside the micelles) was not accounted for.[57] Notably, the structure model fitted to the hydrogenous-SDS system was not validated with contrast matching data from deuterated-SDS.[57] Another report of SANS data for SDS + 3% Pluronic F127 at various SDS concentrations included no proper analysis, qualitative or quantitative.[64]

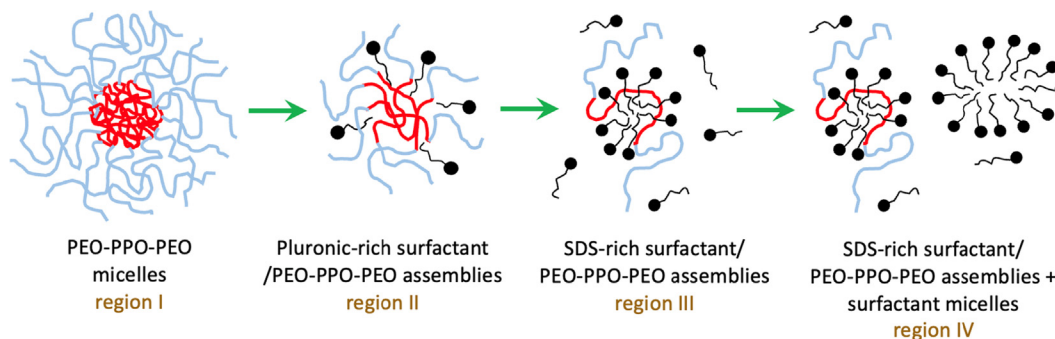


Fig. 1. Schematic of association in aqueous solution between SDS and PEO-PPO-PEO block copolymer above the block copolymer CMC, when increasing amounts of ionic surfactant are added to the polymer solution of fixed concentration. Regions I, II, III and IV correspond to different stages of PEO-PPO-PEO block copolymer and ionic surfactant interactions.[55] In region I there is no detectable association between SDS molecules and Pluronic micelles. In region II, SDS associates with Pluronic micelles to form Pluronic-rich SDS + Pluronic assemblies; these decrease in size and Pluronic association number with increasing SDS concentration. In region III, SDS associates with Pluronic unimers to form SDS-rich SDS + Pluronic assemblies. In region IV, polymer-free SDS micelles also form in the aqueous solution.

The present SANS study addresses limitations of the previous studies and, on the basis of contrast matching using deuterated-SDS, concludes on a definitive structure and composition of SDS + Pluronic assemblies (mixed micelles), a composition that is different than what was previously reported, but is consistent with a variety of experimental observations.

In what follows, we start by justifying the structure model for SDS-rich SDS + Pluronic assemblies that was employed here in the analysis of SANS intensity data, and then proceed to discuss how the structure and composition of these mixed micelles are affected by the surfactant concentration (for a fixed Pluronic type) and the PEO-PPO-PEO block copolymer type (Pluronic F127 or P123), and what are the factors that influence the structure of mixed micelles formed by ionic surfactant and nonionic block copolymer.

3.1. Structure of SDS-rich SDS + Pluronic mixed micelles

The structure + interactions model that best fits the scattering originating from SDS-rich SDS + Pluronic assemblies is the combination of the core-shell ellipsoid form factor and Hayter rescaled mean spherical approximation (RMSA) structure factor with the correlation length model.

Regarding the micelle composition, upon testing the previously considered[57] scenario with the micelle core consisting only of SDS alkyl chains and the micelle shell comprising SDS headgroups, counterions, Pluronic PO and/or EO segments, and associated water of hydration, we were not able to obtain a set of parameters that fitted well data from both h-SDS and d-SDS systems (at the same overall composition) (refer to [Supplementary Information](#)). Specifically, in scenario number 1, the scattering length density of the mixed micelle core ρ_{core} for d-SDS systems should be equal to the scattering length density of $\text{CD}_3(\text{CD}_2)_{11}$ alkyl chains. With this ρ_{core} value, the model (equations 3–8) was not able to fit the SANS intensity curves of the d-SDS systems. Hence we can eliminate scenario number 1 for the composition of SDS-rich SDS + Pluronic assemblies. The fits for the d-SDS + Pluronic in D_2O system improved when the ρ_{core} value was decreased while fitting the data. For the ρ_{core} value to be lower than the SLD of $\text{CD}_3(\text{CD}_2)_{11}$, PO segments should be included in the micelle core. Hence, we tried fitting SANS data considering scenario number 2 with the mixed micelle core consisting of SDS alkyl chains and some Pluronic PO segments. Scenario number 2 fitted both h-SDS data and d-SDS data with a set of reasonable parameters (reported in [Supplementary Information](#)). However, the presence of Pluronic PO segments in the core of the mixed micelle raises the likelihood of some hydration water being present there. Indeed, fits to our SANS

data allowing some water in the micelle core as a fitted parameter lead to physically realistic hydration of PO segments. SANS and MD studies on Pluronic micelles in water reported compositions that result in hydration numbers in the range 0.7–3.5 for a PO segment located in the core of PEO-PPO-PEO micelles.[13,17,57,74,85]

On the basis of fitting the same set of structural parameters on SANS intensities from both h-SDS-containing and d-SDS-containing systems, and the considerations outlined above, the composition of SDS-rich SDS + Pluronic assemblies that emerges as the most appropriate is that of scenario number 3, with a micelle core consisting of alkyl chains from SDS, PO segments from Pluronic PEO-PPO-PEO block copolymer, and some hydration water, and a micelle shell comprising SDS headgroups, counterions, Pluronic PO and/or EO segments, and associated water of hydration. The remaining PO and/or EO segments reside in the bulk solution.

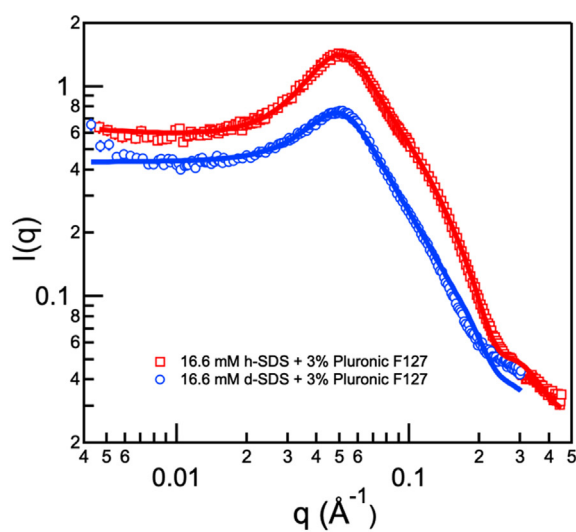
The presence of (i) PEO in the micelle shell and (ii) PPO in the micelle core, and (iii) the number of Pluronic molecules per mixed micelle which we conclude from the analysis of SANS intensity data are consistent with a variety of observations from techniques different than SANS, as discussed below.

1. The interactions between SDS and PEO in the SDS + Pluronic systems of interest to this study are best discussed in the context of studies on homopolymer PEO. MD simulations on SDS + PEO have shown that the PEO resides on the micelle surface and at the hydrocarbon-water interface. In this manner, the unfavorable contact between water and hydrocarbon is reduced and, at the same time, the ether oxygens remain hydrated.[86] This structure/composition of the SDS + PEO mixed micelles is in agreement with the available experimental results for these systems.[70,87]
2. Due to the limited aqueous solubility of PPO homopolymer, SDS + PPO solutions have been studied for only short-chain PPO with an average molar mass 1000 (PO_{14}). The SDS + PPO studies suggested that short-chain PPO can incorporate into SDS micelles and form SDS + PPO mixed micelles, similar to the action of medium chain alcohols.[88–90] 2D NOESY spectra and NMR from aqueous mixtures of Pluronic F127 or P123 and the cationic gemini surfactant hexamethylene-1,6-bis(dodecyl-dimethylammonium bromide) (12–6–12) have shown intermolecular cross-peaks between the alkyl chain protons of 12–6–12 and the methyl and methenyl protons of the PPO blocks.[91] These cross-peaks indicated that the distances between the related protons are not greater than 5 Å and the protons are close enough to couple with each other, suggesting that the PEO-PPO-PEO polymers and 12–6–12 associate mainly

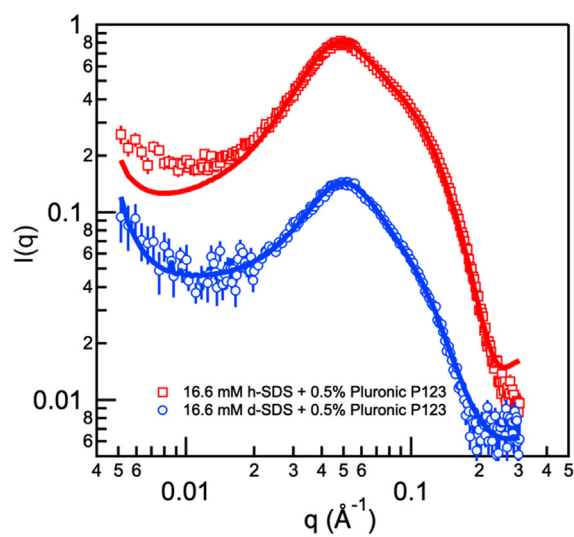
via hydrophobic interaction between the alkyl chains of 12–6–12 and PO segments, consequently the hydrophobic alkyl chains of 12–6–12 and the PPO blocks form the hydrophobic core of micelles.[91] The above experimental evidence supports the mixing in the micelle core of alkyl chains and Pluronic PPO.

3. With PPO present in the core and PEO in the shell of the mixed micelle, the question now is how many Pluronic molecules participate in a mixed micelle. The answer can be inferred from calorimetry data and is confirmed by the SANS analysis presented here. Micellization of PEO-PPO-PEO block copolymers in water is driven by favorable entropy changes and is endothermic.[11,66] Correspondingly, the dissociation of Pluronic micelles is exothermic.[11,66] The enthalpies of micellization ($\Delta H_{m,p}$) of Pluronic F127 and Pluronic P123 at their critical micellization temperature for 1 wt% aqueous solutions are 253 kJ/mol and 329 kJ/mol, respectively.[11] For SDS, the enthalpy of micellization ($\Delta H_{m,s}$) in water is endothermic at

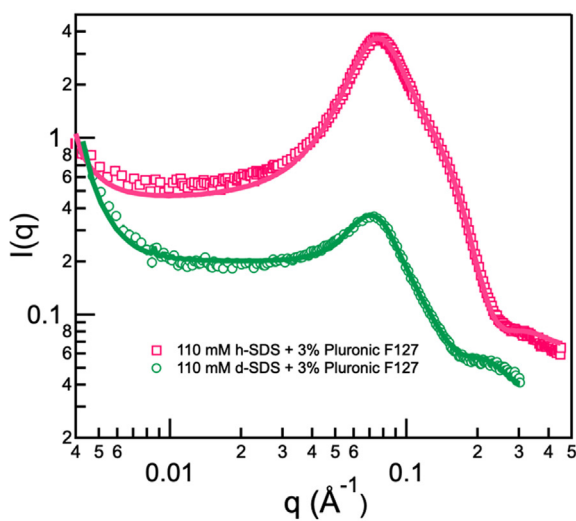
low temperatures (e.g., 4.7 kJ/mol at 15 °C) and turns exothermic at higher temperatures (-7.5 kJ/mol at 40 °C).[46] At the temperature of the present study (22 °C), $\Delta H_{m,s} = 1.3$ kJ/mol,[46] much smaller than $\Delta H_{m,p}$. ITC shows exothermic peaks upon addition of SDS to PEO-PPO-PEO micelles in aqueous solution, which was ascribed to the breakup of Pluronic micelles with the binding of SDS, and accompanying hydration of PO segments.[46,56,59] Dividing the enthalpies of micellization of Pluronic F127 and P123 by their association numbers ($N_{agg,p} = 39$ for Pluronic F127[68] and $N_{agg,p} = 117$ for P123[74]) gives $\Delta H_{m,p}/N_{agg,p} = 6.5$ kJ/mol and 2.8 kJ/mol, respectively. The enthalpy change for the formation of SDS-rich SDS + Pluronic assemblies, reported per mole of SDS ($\Delta H_{r,m}$), was -15 kJ/mol for Pluronic F127 and -4.5 kJ/mol for Pluronic P123, respectively.[46] The dissociation of the block copolymer micelle (which is an exothermic process with enthalpy = minus $\Delta H_{m,p}$) and the interaction between surfactant and polymer



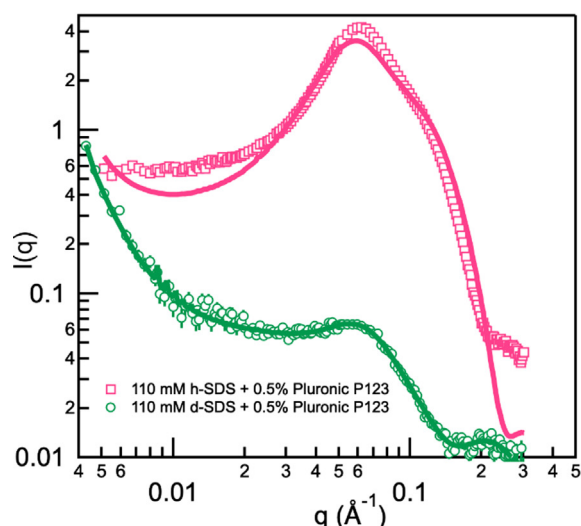
(a)



(a)



(b)



(b)

Fig. 2. SANS intensity data and fits (solid lines) to the combination of the core-shell ellipsoid form factor and Hayter rescaled mean spherical approximation (RMSA) structure factor with the correlation length model for (a) 16.6 mM h-SDS or d-SDS + 3% Pluronic F127 in D_2O , and (b) 110 mM h-SDS or d-SDS + 3% Pluronic F127 in D_2O .

Fig. 3. SANS intensity data and fits (solid lines) to the combination of the core-shell ellipsoid form factor and Hayter rescaled mean spherical approximation (RMSA) structure factor with the correlation length model for (a) 16.6 mM h-SDS or d-SDS + 0.5% Pluronic P123 in D_2O , and (b) 110 mM h-SDS or d-SDS + 0.5% Pluronic P123 in D_2O .

molecules are the major contributors to $\Delta H_{r,m}$. [46] These $\Delta H_{r,m}$ values are approximately double the $\Delta H_{m,P}/N_{agg,P}$ values calculated above, suggesting that the SDS-rich SDS + Pluronic assemblies contain approximately two Pluronic molecules per mixed micelle, which is in agreement with the conclusion of our SANS analysis that is presented below.

In addition to concluding on the structure/composition of the mixed micelles, we established the presence of free (non-associated) polymer in the bulk solution through the need for incorporating in the SANS analysis the correlation length model. For example, in the case of SDS + Pluronic F127 systems, at both 16.6 mM and 110 mM SDS, SANS fits without the correlation length model are unable to capture well the intensities at the low- q region; the same evidence emerged from the analysis of 110 mM SDS + Pluronic P123 SANS data (refer to [Supplementary Information](#)).

SANS intensity data, together with best fits to the structure/composition model described above, are shown in [Figs. 2 and 3](#). Important parameters obtained from fitting SDS + Pluronic SANS data are summarized in [Table 1](#) (the complete set of parameters is provided in SI, Table SI11), while parameters describing polymer-free SDS micelles are presented in [Table 2](#).

3.2. Size and composition of SDS + Pluronic F127 mixed micelles

3.2.1. Low SDS concentration

Starting with the Pluronic F127 systems, the physical picture that emerges for a SDS-rich SDS + Pluronic F127 assembly formed at the lower SDS concentration considered here, 16.6 mM, is that of a core-shell sphere comprising an average of 19 SDS molecules and 2 (~5 vol%) Pluronic F127 molecules. The micelle core consists of

SDS alkyl chains (26 vol%), Pluronic F127 PO segments (49 vol%) and hydration water (25 vol%), while the shell consists of SDS headgroups and counterions (0.3 vol%), Pluronic F127 EO segments (1.9 vol%), and hydration water (98 vol%). The core radius is 18.2 Å, the shell thickness 27.2 Å, and the fractional charge on the micelle 0.65. The SDS volume % is not very high compared to that of Pluronic F127 because the 16.6 mM SDS composition falls into the early stages of SDS-rich SDS + Pluronic F127 assembly formation. At 3% F127 + 16.6 mM SDS, the fraction of Pluronic F127 molecules which do not participate in mixed micelles and are in the bulk aqueous solution is 0.27.

3.2.2. High SDS concentration

At a higher SDS concentration, 110 mM, the SDS-rich SDS + Pluronic F127 assemblies formed are core-shell ellipsoids, comprising on average 40 SDS molecules and 1 (~15 vol%) Pluronic F127 molecule. The micelle core consists of SDS alkyl chains (80 vol%), Pluronic F127 PO segments (17 vol%) and hydration water (3 vol%); the shell consists of SDS headgroups and counterions (5 vol%), Pluronic F127 PO and EO segments (14 vol%), and hydration water (81 vol%). The core radius is 16.7 Å, the shell thickness 8.9 Å, and the fractional charge on a micelle 0.60. Separate from the SDS-rich SDS + Pluronic F127 assemblies, in the bulk solution reside a fraction (0.05) of Pluronic F127 molecules and polymer-free SDS micelles. The shape, size and composition of these free SDS micelles are the same as those of SDS micelles formed in plain water (in the absence of added polymer).

3.2.3. SDS concentration effects

Comparing the two SDS concentrations examined for the Pluronic F127 systems, we note that the SDS association number in the mixed micelles increased 110%, from 19 to 40, and the percentage

Table 1

Important parameters obtained by fitting simultaneously SANS data for h-SDS + 3% Pluronic F127 and d-SDS + 3% Pluronic F127, and for h-SDS + 0.5% Pluronic P123 and d-SDS + 0.5% Pluronic P123 in D₂O, using the correlation length + core shell ellipsoid Hayter MSA model, and considering 2 Pluronic molecules per one SDS + Pluronic mixed micelle at 16.6 mM SDS, and 1 Pluronic molecule per one SDS + Pluronic mixed micelle at 110 mM SDS.

	SDS + 3% Pluronic F127		SDS + 0.5% Pluronic P123	
C_{SDS} (mM)	16.6	110	16.6	110
η	19.0 ± 0.5	40.1 ± 0.9	37.9 ± 3.8	40.9 ± 7.9
α	0.65 ± 0.02	0.60 ± 0.04	0.34 ± 0.03	0.35 ± 0.07
b (Å)	18.2 ± 0.04	16.7	16.7	16.7
δ (Å)	27.2 ± 0.2	8.9 ± 0.1	16.1 ± 2.0	8.4 ± 2.8
ϵ	1.0	0.90 ± 0.02	1.37 ± 0.12	0.80 ± 0.16
R_0 (Å)	45.5 ± 0.2	25.1 ± 0.3	34.7 ± 1.0	24.0 ± 1.5
$n_{PO,core}$	130 ± 2	31 ± 1	113 ± 10	11 ± 2
$n_{PO,shell}$	0	34 ± 1	23 ± 4	58 ± 2
$n_{EO,shell}$	106 ± 1	51 ± 2	0	3 ± 7
f_p	0.50	0.50	0.72	0.75
N_{D2O} per PO, core	1.6	0.5	0.8	0.5
$V_{h, micelle}$	93 ± 1.5	60 ± 1.1	83 ± 11.2	58 ± 12.6
$V_{SDS, core}$	26 ± 0.7	80 ± 2.5	50 ± 6.6	92 ± 25.6
$V_{p, core}$	49 ± 0.8	17 ± 0.7	40 ± 5.0	7 ± 1.9
$V_{h, core}$	25 ± 0.3	3 ± 0.1	10 ± 1.2	1 ± 0.3

η is the surfactant (SDS) association number in the SDS/Pluronic mixed micelle; α fractional charge on a micelle; b micelle core minor radius; ϵ ratio of micelle core major to minor radius; δ micelle shell thickness; R_0 mean spherical radius; $n_{PO,core}$ number of PO segments in the micelle core; $n_{PO,shell}$ number of PO segments in the micelle shell; $n_{EO,shell}$ number of EO segments in the micelle shell; f_p fraction of Pluronic molecule in the SDS/Pluronic mixed micelle (in the case of 16.6 mM SDS + 3% Pluronic F127, 50 vol% of a Pluronic F127 molecule resides in SDS/Pluronic mixed micelle); N_{D2O} per PO, core number of water molecules per PO segment in the micelle core; $V_{h, micelle}$ percentage of micelle volume occupied by water molecules; $V_{SDS, core}$ percentage of micelle core volume occupied by SDS; $V_{p, core}$ percentage of micelle core volume occupied by Pluronic molecule; $V_{h, core}$ percentage of micelle core volume occupied by water molecules.

Table 2

Important parameters that fit SANS data of polymer-free SDS micelles at 110 mM SDS.

C_{SDS}	η_s	α_s	b_s (Å)	δ_s (Å)	ϵ_s
110 mM	83.7 ± 0.5	0.24 ± 0.002	16.68	6.06	1.51 ± 0.01

η_s is the surfactant (SDS) association number in polymer-free SDS micelles; α_s fractional charge on a free SDS micelle; b_s minor core radius of free SDS micelles; δ_s shell thickness of free SDS micelles; ϵ_s ratio of micelle core major to minor radius in free SDS micelles.

of the micelle core volume occupied by SDS increased from 26% to 80%, following a 7-fold increase in the SDS concentration from 16.6 to 110 mM (Fig. 4). The increases in the SDS association number and in the mixed micelle volume fraction occupied by SDS, as observed in our SANS results, reflect an increasing number of SDS molecules that bind to the polymer due to hydrophobic effect, until the polymer becomes saturated with the surfactant, upon increasing the SDS concentration at fixed polymer content.

Upon increasing SDS from 16.6 to 110 mM, the SANS parameters obtained show that the percentage of the micelle core volume occupied by Pluronic F127 molecule(s), or the number of PO segments residing in the hydrophobic micelle core, decrease significantly, from 49% to 17%. At the higher SDS concentration, most of the polymer chain resides in the micelle shell and aqueous solution, and only a few PO segments reside in the micelle core. The increased number of SDS molecules in the mixed micelle tends to increase the electrostatic repulsions between the surfactant headgroups and the dehydration of the Pluronic molecules. The move of some PO segments from the micelle core to the shell decreases the electrostatic repulsions between the surfactant headgroups, while the ether oxygens of the polymer rehydrate in the micelle shell. While the internal composition changed, the fraction of a Pluronic F127 molecule that resides in a SDS micelle (i.e., the ratio of the volume of F127 that resides in a SDS micelle to the total volume of a Pluronic F127 molecule) remained almost the same.

An additional effect of increasing SDS from 16.6 to 110 mM is the shrinkage of the mixed micelles: their volume decreased by 83%, and the size decreased by 45%. These decreases are ascribed to the decrease in the number of Pluronic F127 molecules per mixed micelle, from 2 to 1, and the corresponding decrease in the hydration water. The percentage of the micelle core volume occupied by water decreased from 25% to 3% between 16.6 mM and 110 mM SDS. The decrease in the water content of the mixed micelles suggests an increase in the hydrophobicity. This is in agreement with the decrease in the pyrene fluorescence I_1/I_3 ratio observed upon increasing the SDS concentration from 16.6 mM to 110 mM,[55] and the endothermic dehydration of Pluronic molecules with the binding of SDS.[46,59]

3.2.4. Mixed micelle – free micelle comparison

Comparing the mixed micelles to Pluronic-free SDS micelles (Table 2), we note that the SDS association number in the SDS-rich SDS + Pluronic F127 assemblies (40) is half that in free SDS micelles (84). The fractional charge on a mixed micelle is 2.5 times that on a free SDS micelle, indicating greater counterion dissociation in SDS-rich SDS + Pluronic F127 assemblies compared to free SDS micelles. This agrees with our conductivity results.[55] The greater counterion dissociation in SDS-rich SDS + Pluronic F127 assemblies could be due to the polymer “diluting” the headgroup charges, thus less of a need for counterion “condensation”, and a bigger fraction of counterions are free to come and go in the solution.

3.2.5. Block copolymer – homopolymer comparison

Comparing SDS + PEO-PPO-PEO block copolymer mixed micelles to SDS + PEO homopolymer mixed micelles in aqueous solution, we note that, while the structure (association number, shape and size) of SDS micelles bound to PEO is typically similar to the structure of free SDS micelles,[70] the composition of the SDS + Pluronic mixed micelles differs in that polymer with associated water of hydration are present in the micelle core. Clearly, the hydrophobic PO segments prefer to locate inside the micelle core

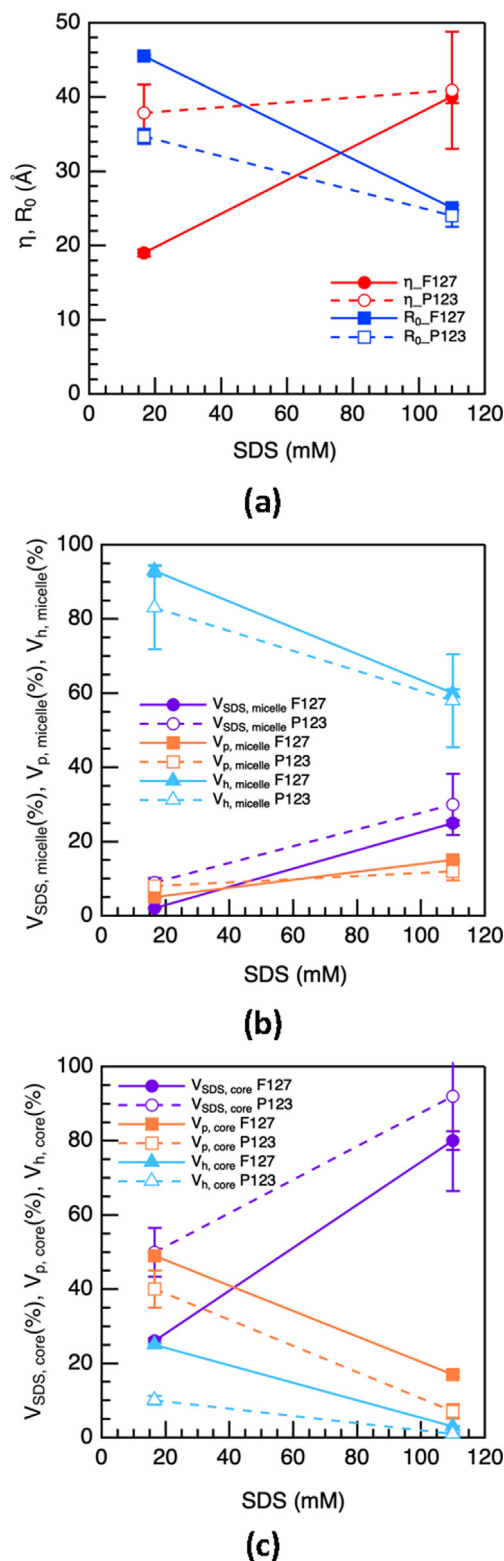


Fig. 4. Mixed micelle structure and composition parameters obtained from analysis of SANS data, plotted as a function of surfactant concentration for SDS + Pluronic F127 (solid lines) and SDS + Pluronic P123 (dotted lines) systems: (a) number of SDS molecules per mixed micelle (η), and mean spherical radius of mixed micelle (R_0); (b) percentage of the mixed micelle total volume occupied by SDS ($V_{SDS, micelle}$), by polymer ($V_{p, micelle}$) and by hydration water ($V_{h, micelle}$); (c) percentage of the mixed micelle core volume occupied by SDS ($V_{SDS, core}$), by polymer ($V_{p, core}$) and by hydration water ($V_{h, core}$).

and, because of the ether oxygens, some water may accompany them. The hydrophobic driving force for locating PPO in the micelle interior is consistent with the much lower critical association concentration values (CAC: surfactant concentration where surfactant molecules start binding to polymer chains) of SDS with unassociated PEO-PPO-PEO block copolymer, compared to the CAC values of SDS in aqueous PEO homopolymer solution.[55,59]

It is interesting to note that the SDS association number in the SDS-rich SDS + Pluronic F127 assemblies (40) is half that in free SDS micelles (84), whereas the SDS association number in PEO-bound SDS micelles is typically similar to the association number of polymer-free SDS micelles. This can be ascribed to the hydrophobicity of the polymer. The surfactant association number in polymer-bound micelles decreases as the polymer hydrophobicity increases since the free energy change associated with the adsorption of one polymer segment from water to the micellar hydrocarbon core-water interface becomes more negative.[92] If a polymer is more hydrophobic, then a larger portion of the area at the micellar core-water interface is occupied by polymer segments, which, in turn, generates stronger steric repulsions between the surfactant headgroups present at the interface. These stronger repulsions force the surfactant headgroups further apart, thus leading to the formation of smaller micelles.[92] This picture is consistent with the experimental observation[93] that micelles bound by PPO are smaller than those bound by PEO (since PPO is more hydrophobic than PEO).[92]

3.3. Size and composition of SDS + Pluronic P123 mixed micelles

3.3.1. Low SDS concentration

The mixed micelles formed in the Pluronic P123 systems exhibit scattering that is best fitted with the same models as in the Pluronic F127 systems. At 16.6 mM SDS, the SDS-rich SDS + Pluronic P123 assemblies are core-shell ellipsoids, comprising on average 38 SDS molecules and 2 (~8 vol%) Pluronic P123 molecules. The core consists of SDS alkyl chains (50 vol%), Pluronic P123 PO segments (40 vol%) and hydration water (10 vol%); the shell consists of SDS headgroups and counterions (2.0 vol%), Pluronic P123 PO and EO segments (1.5 vol%), and hydration water (96.5 vol%). The micelle core minor radius is 16.7 Å, the shell thickness 16.1 Å, and the fractional charge on a micelle 0.34. The fraction of Pluronic P123 molecules that exist in the aqueous solution separate from mixed micelles is almost zero.

3.3.2. High SDS concentration

At the higher SDS concentration (110 mM), the SDS-rich SDS + Pluronic P123 assemblies are core-shell ellipsoids, comprising 41 SDS molecules and 1 (~12 vol%) Pluronic P123 molecule. The core consists of SDS alkyl chains (92 vol%), Pluronic P123 PO segments (7 vol%) and hydration water (1 vol%); the shell consists of SDS headgroups and counterions (7 vol%), Pluronic P123 PO and EO segments (14 vol%), and hydration water (79 vol%). The core radius is 16.7 Å, the shell thickness is 8.4 Å, and the fractional charge on a micelle is 0.35. Coexisting with SDS-rich SDS + Pluronic P123 assemblies, in the bulk solution are a fraction (0.22) of Pluronic P123 molecules and polymer-free SDS micelles. The shape, size and composition of these free SDS micelles are the same as the SDS micelles formed in plain water (in the absence of added polymer).

3.3.3. SDS concentration effects

Comparing the two SDS concentrations for the Pluronic P123 systems, we note that the SDS association number in the mixed micelles increased by 8%, from 38.0 at 16.6 mM SDS to 41 at 110 mM SDS. The fractional charge on a mixed micelle remained almost the same. The volume of an SDS-rich SDS + Pluronic P123

assembly decreased by 67%, and the size decreased by 31%, when the SDS concentration increased from 16.6 mM to 110 mM. The fraction of a Pluronic P123 molecule that resides in an SDS micelle remained almost the same. The percentage of the whole micelle volume occupied by SDS in an SDS-rich SDS + Pluronic P123 assembly increased from 9% to 30%, and the percentage of whole micelle volume occupied by Pluronic P123 increased from 8% to 12%, while the percentage of whole micelle volume occupied by water decreased from 83% to 58% between 16.6 and 110 mM SDS. The percentage of the micelle core volume occupied by SDS in an SDS-rich SDS + Pluronic P123 assembly increased from 50% to 92%, while the percentage of the micelle core volume occupied by Pluronic P123 decreased from 40% to 7%, and the percentage of the micelle core volume occupied by water decreased from 10% to 1% between 16.6 and 110 mM SDS. The decrease in the percentage of water in SDS-rich SDS + Pluronic P123 assemblies is consistent with the observed decrease in the pyrene fluorescence I_1/I_3 ratio.[55]

3.3.4. Mixed micelle – free micelle comparison

Comparing the SDS + Pluronic P123 mixed micelles to Pluronic-free SDS micelles, we note that the SDS association number in the mixed micelles (41) is half that in free SDS micelles (84). The fractional charge on an SDS + Pluronic P123 assembly is 1.5 times that on a free SDS micelle, indicating greater counterion dissociation in SDS-rich SDS + Pluronic P123 assemblies, in agreement with conductivity results.[55]

3.4. Comparison of SDS + Pluronic F127 and SDS + Pluronic P123 mixed micelles

3.4.1. Low SDS concentration

At the lower SDS concentration considered here (16.6 mM), several differences are observed between mixed micelles formed by Pluronic F127 and those formed by Pluronic P123 (refer to Table 1 and Fig. 4): the volume of a SDS + Pluronic F127 micelle is 2.2 times the volume of a SDS + Pluronic P123 micelle, while the volume of the core of a SDS + Pluronic F127 micelle is almost equal to that of a SDS + Pluronic P123 micelle; the SDS association number in Pluronic F127 micelles is half of that in SDS + Pluronic P123 micelles; the volume occupied by SDS (26%) inside SDS + Pluronic F127 micelle core is 1/2 of the volume occupied by SDS (50%) inside SDS + Pluronic P123 micelle core; the fraction of a Pluronic F127 molecule (0.50) residing inside a mixed micelle is 0.7 times the fraction of a Pluronic P123 molecule (0.72) in a mixed micelle; the fractional charge (0.65) on a SDS + Pluronic F127 micelle is twice the fractional charge (0.34) on a SDS + Pluronic P123 micelle. The SANS results obtained show that the water content is lower in SDS + Pluronic P123 micelles compared to SDS + Pluronic F127 micelles, suggesting a more hydrophobic environment in SDS + Pluronic P123 micelles. This is consistent with the lower pyrene fluorescence intensity I_1/I_3 ratios obtained in SDS + 0.5% Pluronic P123 aqueous solutions compared to SDS + 3% Pluronic F127 aqueous solutions.[55] The decrease in the water content in both SDS-rich SDS/Pluronic F127 or P123 assemblies with the increase in SDS concentration from 16.6 mM to 110 mM is also consistent with the decrease in the pyrene I_1/I_3 ratio of SDS + Pluronic F127 or P123 aqueous solutions with increased SDS concentration.[55] The main similarities between mixed micelles formed by Pluronic F127 and those formed by Pluronic P123 are the two Pluronic molecules per one mixed micelle and the similar volume occupied by Pluronic F127 (5%) and Pluronic P123 (8%) in the SDS + Pluronic micelles.

The many differences observed between SDS + Pluronic F127 and SDS + Pluronic P123 mixed micelles at the lower SDS concentration (16.6 mM) can be attributed to the different SDS concentra-

tions ranges where the formation of SDS-rich SDS + Pluronic assemblies takes place (region III, Fig. 1[55]). For SDS + Pluronic F127, the region III concentration range is 2.5–100 mM, whereas for SDS + Pluronic P123 it is 4–25 mM.[55] At 16.6 mM SDS, the formation of SDS-rich SDS/Pluronic F127 assemblies is at the early stage relative to the 2.5–100 mM SDS range, while the SDS-rich SDS/Pluronic P123 assemblies are near to saturation (relative to the 4–25 mM SDS range). The greater water content of the SDS + Pluronic F127 assemblies compared to SDS + Pluronic P123 assemblies observed in our SANS results could be ascribed to the greater rehydration of the more hydrophilic Pluronic F127 compared to Pluronic P123. This is related to the more exothermic enthalpy change (reported per mole of polymer) for Pluronic F127 (–134 kJ/mol), compared to Pluronic P123 (–100 kJ/mol), for the formation of SDS-rich SDS + Pluronic mixed micelles (region III) after mixing block polymer micelles and surfactant micelles.[46] At the lower SDS concentration, the SDS-to-Pluronic molecular ratios in the mixed micelles are 9.5 and 19 for Pluronic F127 and Pluronic P123, respectively. These ratios obtained from the present SANS analysis are in excellent agreement with the number of SDS molecules per polymer chain required to disintegrate Pluronic micelles (9 for F127, 22 for P123) observed from ITC (i.e., at the end of the exothermic peak in SDS + Pluronic ITC curves).[46] For both SDS + Pluronic F127 and SDS + Pluronic P123 systems, the higher SDS concentration 110 mM falls inside region IV demarcated in our recent study,[55] where Pluronic molecules are saturated with surfactant, and coexist with free SDS micelles in the aqueous solution.

3.4.2. High SDS concentration

At the higher SDS concentration considered here (110 mM), many similarities are observed between Pluronic F127 and Pluronic P123 mixed micelles: one Pluronic molecule per mixed micelle; SDS association number, micelle core minor radius, and shell thickness that are close in both F127 and P123 mixed micelles; both F127 and P123 mixed micelles coexist with free SDS micelles in the solution.

Since the SDS-rich SDS + Pluronic assemblies are above saturation at 110 mM SDS, only a few differences are observed between SDS + Pluronic F127 and SDS/Pluronic P123 mixed micelles: the fraction of a Pluronic molecule that resides in a SDS micelle is greater for Pluronic P123 (0.75) compared to Pluronic F127 (0.50), which could be ascribed to the greater hydrophobicity of Pluronic P123; the PO segments in the core are fewer in SDS + Pluronic P123 mixed micelles compared to SDS + Pluronic F127 mixed micelles. As discussed previously, an increased SDS association number in the micelles would increase the electrostatic repulsions between the surfactant headgroups and, in order to counteract this, some PO segments may move from the micelle core to the shell. Since Pluronic F127 has longer PEO chains compared to Pluronic P123, Pluronic F127 can more effectively reduce the headgroup repulsions in the micelle shell and, hence, a greater number of PO segments are present in the micelle core for Pluronic F127. SDS + Pluronic F127 mixed micelles have greater counterion dissociation or fractional charge (1.7 times) than SDS + Pluronic P123 micelles. This could be ascribed to greater number of PO and EO segments per SDS headgroup present in the shell of a SDS + Pluronic F127 mixed micelle.

3.4.3. Comparison of SDS concentration effects

Comparing the SDS concentration effects for SDS-rich SDS + Pluronic F127 and SDS + Pluronic P123 assemblies, we note that all such effects observed here are the same in both Pluronic F127 and P123.

At both 16.6 mM and 110 mM SDS concentrations, both the total number of PO and EO segments per mixed micelle ($n_{\text{PO,core}} +$

$n_{\text{PO,shell}} + n_{\text{EO,shell}}$) and the number of PO and EO segments per SDS molecule in a mixed micelle ($(n_{\text{PO,core}} + n_{\text{PO,shell}} + n_{\text{EO,shell}})/\eta$) are greater for Pluronic F127 compared to Pluronic P123. This could be ascribed to the bigger size of the Pluronic F127 molecule, i.e., 2.5 times greater number of PO and EO segments, compared to Pluronic P123; thus, there are more F127 segments per mixed micelle.

At the lower SDS concentration (16.6 mM), SDS + Pluronic P123 mixed micelles contain more SDS molecules compared to SDS + Pluronic F127 mixed micelles. This is due to the greater number of polymer segments per mixed micelle and the lower number of SDS molecules per mixed micelle in the case of Pluronic F127. This suggests stronger binding of SDS to Pluronic P123, which is also supported by calorimetry. The enthalpy change for the formation of SDS-rich SDS + Pluronic assemblies from block polymer micelles and surfactant micelles, per mole of polymer segment, was more exothermic for Pluronic P123 (–0.93 kJ/mol EO or PO segment) than Pluronic F127 (–0.51 kJ/mol EO or PO segment).[55]

4. Conclusions

Addition of increasing amounts of ionic surfactants to micelles formed in water by nonionic PEO-PPO-PEO block copolymers (Pluronics) results in surfactant association with the block copolymer micelles, followed by decreases in their size and the number of block copolymers per micelle, a transition into mixed micelles having majority ionic surfactant, and the formation of polymer-free surfactant micelles above the point of saturation of PEO-PPO-PEO molecules with the ionic surfactant.[55] The structure of the surfactant + polymer mixed micelles has remained elusive and forms the motivation for this study.

Mixed micelles formed in aqueous solutions between nonionic amphiphilic polymers Pluronic F127 (EO₁₀₀PO₆₅EO₁₀₀) and Pluronic P123 (EO₁₉PO₆₉EO₁₉) and ionic surfactant SDS are characterized here using SANS. SANS data with contrast matching are analyzed considering various scenarios for the mixed micelle composition, and the resulting parameters reveal the effect of polymer hydrophobicity and surfactant concentration on the structure/composition of the SDS + Pluronic assemblies formed.

The structure and composition of SDS + Pluronic mixed micelles in the SDS-rich region[55] that emerges as the most appropriate is that of a core consisting of SDS alkyl chains, Pluronic PO segments and some water of hydration, and a shell comprising SDS headgroups, counterions, Pluronic PO and/or EO segments, and associated water of hydration. Due to hydrophobic interactions, the PO segments prefer to locate inside the micelle core along with SDS hydrocarbon chains and, because of the ether oxygens, some water may accompany them. The presence of PPO in the micelle core is in accord with NMR results from aqueous mixtures of Pluronic F127 or P123 and a cationic surfactant.[91] The presence of PEO at the micelle shell reduces the unfavorable contact between water and hydrocarbon, and also ensures the hydration of ether oxygens.[86] At the lower SDS concentration, the two Pluronic molecules per mixed micelle obtained here from SANS are consistent with the enthalpy change for the formation of SDS + Pluronic mixed micelles.[46] Further, for both Pluronic F127 and P123, the SDS-to-Pluronic molecular ratios in the mixed micelles obtained from the present SANS analysis are in excellent agreement with the number of SDS molecules per corresponding polymer chain that are required in order to disintegrate Pluronic micelles.[46]

Upon increase in the SDS concentration from 16.6 to 110 mM, the number of PEO-PPO-PEO molecules per SDS + Pluronic mixed micelle decreases from two to one, the surfactant association number increases, and the volume and size of the mixed micelles decrease. The increase in the SDS concentration increases the num-

ber of SDS molecules that bind to the polymer due to hydrophobic effect, thereby leading to stronger electrostatic repulsions between surfactant headgroups, and to the dehydration of PEO-PPO-PEO molecules. To counteract the electrostatic repulsions between headgroups, some PO segments move from the micelle core to the shell. The shrinkage of the mixed micelles is connected to the decrease in the number of Pluronic F127 molecules per mixed micelle from two to one, and the corresponding decrease in the water of hydration.

The polymer hydrophobicity influences the surfactant + polymer assembly structure. The SDS association number in SDS + Pluronic mixed micelles is half of that in free SDS micelles. This differs from SDS micelles bound to PEO homopolymer, which typically have similar structure of free SDS micelles.[70] The fraction of a PEO-PPO-PEO molecule residing in a mixed micelle with SDS is greater for Pluronic P123 (0.75) compared to Pluronic F127 (0.5), and the water content is lower, which could be ascribed to the greater hydrophobicity of Pluronic P123 and its stronger binding of SDS.

The present study of same-composition samples prepared with either h-SDS or d-SDS, and the fits of the two same-composition but different-contrast data-sets with the same models and parameters, enables the validation of the structure and composition of the mixed micelles in a manner that was not previously possible. [57] Moreover, this is the first report on structural/composition information for SDS-rich SDS + Pluronic P123 assemblies. A comparison of assemblies formed between SDS and PEO-PPO-PEO amphiphilic polymers with low and high PEO/PPO ratio is useful in order to probe the effect of polymer hydrophobicity on the mixed micelle structure.

Fundamental insights are thus obtained on the organization of nonionic block copolymers and ionic surfactants in aqueous solutions. Such insights benefit the diverse applications of multi-component complex fluids. For example, the intermixing in the micelle core of alkane and polyether, and the presence of water of hydration (not obvious that these would have been the case) are relevant to the encapsulation capacity of mixed micelles for various compounds, both hydrophobic and hydrophilic. The presence of polymer bound to the micelle but also extending out into the solution allows for micelle-reinforced physical entanglements for high MW polymers, and for steric stabilization and repulsive interactions in the case of low MW polymers. It would be interesting to explore further the effect of surfactant charge (anionic vs. cationic), surfactant hydrophobicity (hydrogenated vs. fluorinated), polymer hydrophobicity (PPO vs. alkyl blocks), and solvent hydrophobicity (plain water vs. water containing additives such as alcohols) on the surfactant + polymer assembly structure and interactions.

CRediT authorship contribution statement

Samhitha Kancharla: Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Dmitry Bedrov:** Funding acquisition, Writing – review & editing. **Marina Tsianou:** Funding acquisition, Conceptualization, Supervision, Writing – review & editing. **Paschalis Alexandridis:** Funding acquisition, Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2021.10.176>.

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