Glucose-Induced Sphere to Ellipsoid Transition of Polyoxyethylene-Polyoxypropylene Block Copolymer Micelles in Aqueous Solutions

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Abstract

The structure of micelles formed by a representative polyoxyethylene-polyoxypropylene-polyoxyethylene amphiphilic block copolymer (Pluronic P105, $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$) in aqueous glucose solution has been probed with the help of viscosity and small angle neutron scattering (SANS) measurements. In the presence of glucose (40 wt%), the relative viscosities of the aqueous block copolymer solutions increase significantly (10 to 100 times) above 50 °C for 1 wt% and above 40 °C for 8 wt% block copolymer, whereas in the absence of glucose the relative viscosities remain almost constant. The macroscopic information obtained by viscosity is elucidated by structural information on the micelles obtained by fitting SANS data to a core-corona prolate ellipsoid form factor. The addition of glucose in aqueous $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ solutions results in micelle growth from sphere to ellipsoid (cigar-like) with major/minor radius ratio in the range 2 to 5. The onset of the sphere-to-ellipsoid shape transition discerned by SANS corresponds to the onset of the solution viscosity increase. In comparison, the shape of micelles formed in binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water solutions remains almost independent of temperature. The observed changes in the micelle structure can be attributed to enhanced dehydration of polyoxyethylene caused by glucose. These findings are relevant to waterborne formulations incorporating polyoxyethylene-containing amphiphiles.

Keywords: block copolymer; Pluronic; Poloxamer; poly(ethylene oxide) (PEO); poly(propylene oxide) (PPO); micelle; small-angle neutron scattering (SANS); viscosity; formulation.

Introduction

The structure of micelles formed by amphiphiles in aqueous solution has been widely studied to order to further our fundamental understanding and to develop various practical applications of such versatile self-assembling systems. In nonionic surfactant systems the micelle shape is often dependent on temperature. For example, micelles formed in aqueous solutions by the nonionic surfactants polyoxyethylene(5)-dodecylether [1], polyoxyethylene(6)-hexadecylether [2,3], and sucrose laurate [4] change shape from sphere to rod with increasing temperature. The micelle shape can also be affected by varying the solvent properties [5-13]. The synergistic effects of solvent quality and temperature can be very important in modulating the self-assembly of nonionic amphiphiles in aqueous solutions.

It has been reported that the micelle shape can change from sphere to ellipse or rod by the addition of alcohols (such as butanol, pentanol, hexanol, heptanol, octanol or benzyl alcohol) to aqueous solutions of ionic surfactants (such as sodium dodecyl sulfate or dodecyltrimethylammonium bromide [6-9]), nonionic surfactants (such as alkyl glucoside [10] or polyoxyethylene(23) lauryl ether [11]), or betaine surfactants (such as laurylsulfobetaine [12]). It is also known that the addition of glycerol or sorbitol to nonionic surfactants such as monoalkyl polyoxyethylene glycols can change the micelle shape from sphere to rod, with a length that increases at first with temperature and then decreases close to the surfactant cloud point (i.e., macroscopic phase separation) [13].

In the case of aqueous solutions of polymeric surfactants such as poly(dimethylsiloxane)-graft-polyether copolymers, an increase in temperature and/or the addition of 2-butoxyethanol, poly(ethylene glycol), glucose, or glycerol cause micelle shape changes from sphere to ellipse or prolonged ellipse, similarly with low-molecular weight surfactants [14-16]. By changing the solvent polarity (quality), polymeric surfactants have the

potential to self-assemble into more complex shapes due to their higher molecular weight and structural flexibility [17,18].

Among the best studied polymeric surfactants are members of the polyoxyethylene-polyoxypropylene-polyoxyethylene (POE-POP-POE) block copolymer family, commercially available as Pluronics or Poloxamers. We have previously reported on the micelle structure of a representative POE-POP-POE block copolymer (Pluronic P105, $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$) in aqueous solutions containing formamide, glycerol, or ethanol [19]. The micelles formed by POE-POP-POE block copolymers in aqueous solutions are usually spherical [19-30], whereas non-spherical micelle shapes are less common [31]. Evidence for rod-like micelles has been reported for the following POE-POP-POE block copolymers in plain water or in aqueous salts solutions: Pluronic P85 ($\text{EO}_{25}\text{PO}_{40}\text{EO}_{25}$) [32-36], Pluronic P94 ($\text{EO}_{28}\text{PO}_{48}\text{EO}_{28}$) [37], Pluronic F127 ($\text{EO}_{99}\text{PO}_{65}\text{EO}_{99}$) [22], Pluronic F88 ($\text{EO}_{103}\text{PO}_{39}\text{EO}_{103}$) [38], Pluronic F87 ($\text{EO}_{67}\text{PO}_{39}\text{EO}_{67}$) [35], and Pluronic L64 ($\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$) [39].

In this paper, we focus on the shape and size modulation of micelles formed by Pluronic P105 ($\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$) block copolymers. Such modulation occurs by means of adding glucose to the aqueous block copolymer solution, and is probed at varying temperatures. The presentation of results and discussion is organized as follows: First we provide macroscopic evidence on solution structure from phase behavior, viscosity, and small-angle neutron scattering (SANS) intensity; then we obtain microscopic details from analysis of SANS data; last, but not least, we discuss the molecular mechanism behind the change of micelle shape. The work reported here is relevant in furthering the fundamental understanding of controlling self-assembly, and also in several processes and products, where structural and rheological changes originating from surfactant self-assembly are directly related to their function.

Results and Discussion

Macroscopic observations: Glucose effect on micelle formation and viscosity

The temperature-concentration phase diagram for the micellization of $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ in aqueous glucose solutions is shown in Figure 1 (these data have been determined from light scattering measurements). At the block copolymer concentration and solution temperature region below the micellization boundary (for a given glucose concentration), the block copolymers remain in solution as individual coils (unimers) [40]. At concentrations and temperatures above the micellization boundary, the block copolymers self-assemble to form micelles (that coexist in equilibrium with unimers). With increasing glucose content, the micellization boundary shifts toward the lower left corner of the diagram (Figure 1). The fact that glucose promotes micelle formation has been attributed to an enhancement of water structure caused by glucose [41] or to the dehydration of polyoxyethylene by glucose (similarly to the case of glycerol [19]). Both mechanisms are plausible, but the dehydration of POE by glucose appears more likely because glucose does not reportedly perturb the water structure up to 50 wt% [42].

Such a dehydration of the POE blocks of POE-POP-POE block copolymers caused by glucose may lead to a micelle shape change. It is well known that a temperature increase can cause the shape of micelles formed by typical POE-containing nonionic amphiphiles in aqueous solution to evolve from spherical to elongated, due to a decrease of the interfacial curvature effected by the dehydration of POE groups [43]. Such a micelle shape change can be connected to a change of the viscosity of the micellar solution [32,39]. For example, the specific viscosity of 0.5 - 4 wt% Pluronic P85 ($\text{EO}_{25}\text{PO}_{40}\text{EO}_{25}$) in 5.5 wt% KF aqueous solution increased by a factor of 10 with temperature increasing from 35 to 41 °C due to a micelle shape change from sphere to rod as was independently confirmed in this case by sedimentation and light scattering

measurements [32]. In another example, intrinsic viscosities for Pluronic P85 or L64 ($\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$) in aqueous KBr, KCl, or KF solutions showed a steep rise (by a factor of 10) with increasing temperature at about 10 - 20 °C below the cloud point [39].

Motivated by the above, we carried out viscosity measurements in order to explore a possible micelle shape change in aqueous $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ glucose solutions. As seen in Figure 2(a), the relative viscosities of ternary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - glucose monohydrate - water solutions increase significantly (10 to 100 times) above 50 °C for 1 wt% and above 40 °C for 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$, while the viscosity of the binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water solutions remains almost independent of temperature (or decreases slightly). This viscosity increase is indicative of a micelle shape change from sphere to ellipse or rod [32,39]. In the case of binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water solutions, the micelles remain spherical according to previously published small-angle neutron and light scattering data [19,44,45].

We note that the 1 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ solutions remain homogeneous and optically transparent and isotropic over the whole temperature range considered here. The 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ solutions were isotropic throughout, but exhibited slight birefringence under polarizing light above 55 °C. The birefringence became stronger when the sample was shaken by hand. The structure at this temperature range may be nematic [24,45,46], a type of self-assembly that rarely appears in aqueous POE-POP-POE block copolymer systems [24]. A further increase in temperature may lead to longer rod-like micelles and a transformation of the nematic phase into a hexagonal lyotropic liquid crystalline phase [24,48]. Such phase is stable over the temperature range considered here in binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water systems, but at much higher block copolymer concentrations (47 - 65 wt%) [49].

From viscosity measurements we can only obtain qualitative information on micelle shape changes. Therefore small angle neutron scattering (SANS) experiments were performed

to acquire quantitative structural information in the nanoscale. Before we analyze the scattering patterns in terms of the micelle structure, let us consider the (model-independent) changes in the overall scattering intensity. The relative SANS scattering intensities at $0.02225 \text{ \AA}^{-1}$ (q value at which scattering data obtained from micellar solutions exhibit a maximum; normalized by the intensity at $40 \text{ }^{\circ}\text{C}$) for $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water binary solutions increased gradually with increasing temperature, whereas those for $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - glucose monohydrate - water ternary solutions increased significantly above $50 \text{ }^{\circ}\text{C}$ for 1 wt%, and above $40 \text{ }^{\circ}\text{C}$ for 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ (Figure 2(b)). Note that the SANS intensity jumps occur at the same temperatures where the relative viscosity starts to increase (Figure 2(a)). Such intensity increase can be due to an increase in the micelle concentration and/or size, with the latter being the case here, as discussed in detail in the following section.

Microscopic information: Glucose effect on micelle structure

Microscopic information on the block copolymer micelle structure as affected by glucose has been obtained from fitting to the SANS data the core-corona prolate (cigar-like) ellipsoid form factor and hard sphere interaction structure factor. The core-corona prolate structure emerged as the more appropriate among other possible structures that we have considered (see section on “Comparison between different models used to fit SANS data”). From fits to this model we can extract values for the following parameters: micelle association number ($N_{\text{association}}$), major and minor micelle radii ($R_{2\text{major}}$ and $R_{2\text{minor}}$), major and minor micelle core radii ($R_{1\text{major}}$ and $R_{1\text{minor}}$), and polymer volume fraction in the micelle corona (α_2) (for details see the section on “SANS data analysis”).

Figure 3 shows the evolution with temperature of the micelle association number ($N_{\text{association}}$) in the absence and in the presence of glucose. $N_{\text{association}}$ for ternary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ -

glucose monohydrate - water solutions doubles above 50 °C for the 1 wt% EO₃₇PO₅₈EO₃₇ system and above 40 °C for the 8 wt% system. On the contrary, N_{association} for binary EO₃₇PO₅₈EO₃₇ - water solutions remains relatively constant [19]. We note that, while the micelle structural data are plotted in Figures 3 and 4 vs. temperature, the prime variable of interest is the glucose content (but it has been advantageous from the experimental point of view to fix the solute concentration and vary the solution temperature [40]).

Values for the major and minor micelle radii (R_{2major} and R_{2minor}) for the systems considered above are presented in Figure 4. With increasing temperature, a significant difference emerges on R_{2major} values in the presence or absence of glucose. R_{2major} values for EO₃₇PO₅₈EO₃₇ (1 or 8 wt%) - glucose monohydrate (40 wt%) - water systems increased above 50 °C for 1 wt% and above 40 °C for 8 wt% EO₃₇PO₅₈EO₃₇. But those for EO₃₇PO₅₈EO₃₇ (1 or 8 wt%) - water systems were relatively independent of temperature. On the other hand, R_{2minor} was mostly unaffected by the presence of glucose and remained within the range 50 - 90 Å throughout the temperature range that we considered. Figures 4(c) and 4(d) show major and minor radii of the micelle core (R_{1major} and R_{1minor}) for the same four systems. The trends are the same to that of the major and minor micelle radii shown in Figures 4(a) and 4(b).

The variations of R_{2major} and R_{1major} become more apparent when we examine the ratios R_{1major}/R_{1minor} and R_{2major}/R_{2minor} (see Figures 4(e) and 4(f)). In the presence of 40 wt% glucose, the R_{1major}/R_{1minor} or R_{2major}/R_{2minor} ratios increase (up to 5 times) above 50 °C for 1 wt% and above 40 °C for 8 wt% EO₃₇PO₅₈EO₃₇. In the absence of glucose, these ratios were almost constant and close to unity (i.e., spherical micelle shape) throughout the temperature range considered [19].

Clearly, the block copolymer micelles become elongated in the presence of glucose above a certain temperature, a phenomenon related to a decrease in the interfacial curvature [43].

One way to assess this for our systems would be to focus on the degree of hydration of the micelle corona, the value of which is a direct outcome of the core-corona micelle structure model that we used for SANS data analysis. Figure 5 shows the variation of the polymer volume fraction in the micelle corona (α_2) with temperature, for micelles formed in the ternary EO₃₇PO₅₈EO₃₇ (1 or 8 wt%) - glucose monohydrate (40 wt%) - water and in the binary EO₃₇PO₅₈EO₃₇ (1 or 8 wt%) - water solutions. The α_2 values in the presence of glucose are significantly higher (0.35 - 0.65) than those in plain water (0.2 - 0.3). An increase of α_2 means a decrease of the water content in the POE-rich block copolymer micelle corona. The α_2 value for EO₃₇PO₅₈EO₃₇ - glucose monohydrate - water systems increases with increasing temperature, whereas α_2 for the EO₃₇PO₅₈EO₃₇ - water systems remains relatively constant [19]. Glucose appears to dehydrate the POE blocks relatively stronger at higher temperature [42,50].

In summary, the addition of glucose in aqueous POE-POP-POE block copolymer solutions results in a micelle growth from sphere to a cigar-like ellipsoid keeping constant the minor radius, while the block copolymer micelles retain the same shape (sphere) in plain water.

It is notable that the evolution of the micelle structural parameters summarized in Figures 3 - 5 is very consistent with the changes of relative viscosity discussed earlier (Figure 2(a)). It is well-known that the viscosity of a dispersion of non-interacting spherical objects will increase when their shape becomes rod-like (keeping the same volume fraction of the dispersed phase). The viscosity will increase even more if the objects start interacting [51,52].

To elucidate the relationship between micelle structure change and viscosity change, the solvent (water + glucose) volume per micelle was calculated (based on the number of micelles per unit volume and the volume per micelle) and from this the distance between adjacent micelles was estimated. These results are presented in the schematics of Figure 6 where micelles are spaced apart from each other with a distance that corresponds to the radius of the

solvent volume per micelle at given conditions. This schematic shows clearly that the more pronounced viscosity increase (over 100 times) observed in 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ aqueous glucose solution is due to strong interactions between adjacent elongated micelles (which through their revolution can generate a higher effective volume and bump onto each other).

Molecular origin of glucose - induced micelle shape change

By increasing the temperature of POE-POP-POE block copolymer aqueous solutions, the POP blocks become progressively less water-soluble than POE, and at a certain temperature (critical micellization temperature, CMT [40]) micelles start forming with a relatively “dry” POP core and a hydrated POE corona. With increasing temperature well above the CMT, the POP core becomes drier and at the same time the POE corona becomes less hydrated [19,21,25,26,53]. As a result, a larger number of POE-POP-POE block copolymer molecules can be packed at the interface between hydrophilic and hydrophobic domains, and the interfacial curvature becomes less positive [32,43]. This can cause the micelles to grow; rod-like micelles have been reported where the interfacial curvature became less positive by increase in temperature [22,33,35-38] or by addition of salts [32,38,39]. The spherical shape cannot be retained because the micelle core diameter cannot increase beyond what is allowed by the length of the POP block [24,35,54].

The POE-POP-POE block copolymer micelle shape changes from sphere to ellipsoid or rod can be related to (i) the relative length of the POP and POE blocks [35] and the degree of their hydration which is influenced by (ii) temperature [22,33,35-38], and /or (iii) addition of solutes and/or solvents in the aqueous solution [32,38,39]. Relevant published work is highlighted below.

(i) Micelle shape change from sphere to rod, and persistence of spherical micelles in $\text{EO}_m\text{PO}_n\text{EO}_m$ aqueous solutions have been reported with increasing the POE block length ($m = 6$,

27, 67, 96) at a constant POP block length ($n = 39$) [35]. The longer the POE block relative to POP, the more stable the spherical shape remained, up to high temperatures [55].

(ii) Micelle shape changes from sphere to rod occurred above 56 °C in 10 wt% Pluronic P94 ($\text{EO}_{28}\text{PO}_{48}\text{EO}_{28}$) aqueous solutions [37], and above 70 °C in 1 wt% Pluronic P85 ($\text{EO}_{25}\text{PO}_{40}\text{EO}_{25}$) [33,36]. A relatively high temperature (above 60 °C) is necessary to cause a micelle shape change from sphere to rod for these block copolymers with comparable POE and POP contents. Micelles are spherical in 5 - 8.9 wt% Pluronic F88 ($\text{EO}_{103}\text{PO}_{39}\text{EO}_{103}$) aqueous solutions up to 90 °C [35,38], and in 12 wt% Pluronic F127 ($\text{EO}_{99}\text{PO}_{65}\text{EO}_{99}$) up to 95 °C [22]. Both these block copolymers have high POE content (80 and 70 %).

(iii) Solute or solvent effects on POE-POP-POE micelle shape are less studied. To the best of our knowledge only effects of inorganic salts have been reported. Rod-like micelles of Pluronic F88 form at 42 °C by adding 6.1 wt% K_2CO_3 [38], Pluronic P85 at 38 °C in the presence of 5.5 wt% KF [32], or Pluronic L64 and P85 at 15 - 20 °C below the cloud point in the presence of salts such as KBr, KCl, and KF [39]. These salts apparently cause further dehydration of POE and decrease sufficiently the interfacial curvature for the formation of rod-like micelles at relatively low temperature (around 40 °C).

In the experiments reported here, the micelles formed in binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water solutions remained almost spherical in the temperature range 7 - 60 °C. In the presence of 40 wt% glucose monohydrate, however, the micelles changed from sphere to prolate ellipsoids above 50 °C for 1 wt% and above 40 °C for 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$. In binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water solutions, an increase of temperature up to 60 °C does not sufficiently dehydrate the POE blocks; this is borne in the relatively low polymer volume fractions (0.2 - 0.3) in the micelle corona that have been obtained by SANS (Figure 5). But upon addition of glucose, the dehydration of POE that is reflected in the relatively high polymer volume fractions (0.35 - 0.65)

in the micelle corona (Figure 5) decreased the interfacial curvature sufficiently for the formation of prolate ellipsoid micelles. There may be other possible reasons for this micelle shape change, e.g., an enhancement of water structure by glucose or specific interactions between POE and glucose, but these are deemed not as important as the dehydration of POE. This is because up to 50 wt% glucose does not reportedly perturb the water structure [42]; furthermore, the interactions between glucose and POE are more repulsive than those between glucose and water [56].

Conclusions

The research presented here is a case study of how solutes can modulate the self-assembly structure in amphiphile solutions. In particular we probed the effect of glucose on the micelle structure of the $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ polyoxyethylene-polyoxypropylene amphiphilic block copolymer in aqueous solutions at varying temperatures by a combination of viscosity and SANS measurements. The work reported here is relevant to furthering the fundamental understanding of self-assembling systems in solvent mixtures and also in diverse applications such as pharmaceuticals, skin-care, hair-care, detergents, coatings and inks, where (i) product function and viscosity are intertwined and (ii) polyethoxylates and polyalcohols (the types of molecules that we consider here) are very common ingredients in the formulations.

In the presence of glucose, the relative viscosities of aqueous $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ solutions increase significantly (by 10 to 100 times) above 50 °C for 1 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ and above 40 °C for 8 wt% $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$, while in the absence of glucose the block copolymer solution viscosities remain almost constant relative to temperature.

The onset of solution viscosity increase coincides with that of shape changes detected by SANS. The addition of glucose results in a micelle shape change from sphere to prolate

ellipsoid (cigar-like) that prolonged along major axis with the minor radius kept constant (the major/minor radius ratio increases to 5 within experimental range). The micelles that formed in binary $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ - water systems remain almost the same shape (sphere) relative to temperature.

In the absence of glucose, an increase in temperature up to 60 °C is not sufficient to dehydrate the polyoxyethylene blocks, as indicated by the relatively low (0.2 - 0.3) polymer volume fractions in the micelle corona. Glucose causes dehydration of POE as reflected in the relatively high (0.35 - 0.65) POE volume fractions in the micelle corona, thus decreases the interfacial curvature, and leads to the formation of prolate ellipsoid micelles.

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Materials and Methods

Materials

The Pluronic P105 polyoxyethylene-polyoxypropylene-polyoxyethylene (POE-POP-POE) block copolymer was obtained from BASF Corp. and used as received. According to the manufacturer it has molecular weight of 6500 and 50 wt% POE content and can thus be represented as $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$. Among the various POE-POP-POE block copolymers available commercially, Pluronic P105 is of intermediate hydrophobic/hydrophilic balance and molecular weight. Not coincidentally, it exhibits a rich phase behavior [48,49]. D(+)-glucose monohydrate (>99.5%) was purchased from Fluka Chemical Corp., Milwaukee, WI. Millipore-filtered water was used for sample preparations for phase diagrams and viscosity measurements. The deuterium oxide (99.4%) used for the SANS experiments was purchased from Cambridge Isotope Laboratories, Inc., Tewksbury, MA. All samples were prepared by weighing appropriate amounts of polymer, solute and water. For SANS samples, hydrogenous water (except the water originating from glucose monohydrate) was replaced by 1.11 times its weight with deuterium oxide so that the number of water molecules remains the same. Appropriate time was allowed for thermodynamic equilibration of the samples prior to their testing [57,58]. The dipole moments of glucose and water are 14.1 and 3.11, and the octanol/water partition coefficients $\log P$ -3.29 and -1.38, respectively [59,60]. The densities of aqueous glucose monohydrate solutions were measured by a pycnometer.

Micellization phase boundary measurements

The light scattering intensity of samples used to determine the temperature-concentration micellization boundaries was measured by a Brookhaven BI-200SM

goniometer at 90° with varying temperature using a Lexel model 95 argon ion laser operating at 514 nm. The sample compositions are the following: 1 or 8 wt% Pluronic P105, 0, 20, 30, 40 wt% glucose monohydrate, with the remainder being water. The samples were also observed under polarizing light in the temperature range 7 – 60 °C to check for possible anisotropic (nematic or hexagonal or lamellar liquid crystalline) structure [48,49].

Viscosity measurements

Viscosities of aqueous Pluronic P105 solutions and water-glucose solutions were measured by Cannon-Fenske routine type viscometer [61] at different temperatures. Here we report the relative viscosity which is the viscosity of Pluronic P105 ternary or binary solutions divided by the viscosity of the correspondent solvents (consisting of glucose and water or plain water, respectively).

Small-angle neutron scattering (SANS) experiments

Small-angle neutron scattering was used to determine the micelle structure [15,19-21]. Deuterium oxide was used as a solvent due to its relatively high SLD ($\rho_{D2O} = 6.48 \times 10^{10} \text{ cm}^{-2}$) [19] compared to those of the POP and POE blocks of the copolymer ($\rho_{POP} = 0.325 \times 10^{10} \text{ cm}^{-2}$, $\rho_{POE} = 0.547 \times 10^{10} \text{ cm}^{-2}$) [19]. The measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), beam guide NG3. The neutron wavelength used was 0.6 nm. The samples were placed in 1 mm path length titanium cells with quartz windows. The sample to detector distance was 200 and 1000 cm which allowed us to probe the q -ranges 0.0159-0.3092 and 0.0045-0.0638 $\text{\AA}^{-1}$, respectively. The time for collecting scattering data varied from 5 to 15 min depending on the sample to detector distance. The

temperature varied in the range 30 - 60 °C. The angular distribution of scattered neutrons was recorded in a two dimensional detector. For a given scattering vector value, q^* , the scattering intensity was obtained by averaging the intensity of all the points on the 2-D detector space corresponded to q^* from the central point. Scattering intensities from samples were corrected for detector background, empty cell scattering, and sample transmission [62].

SANS data analysis

The absolute SANS intensity for monodisperse systems can be expressed as a product of the form factor $P(q)$ which describes the structure of particles, in our case micelles, and the structure factor $S(q)$ which describes the interaction between (micelle) particles:

$$I(q) = A N_p P(q) S(q) + B \quad (1)$$

where A is the absolute intensity factor which is used as a free-fitting parameter in order to account for uncertainties in the absolute intensity calibration, N_p is the number density of micelles, and B is a background factor which is another fitting parameter used to account for residual background [62].

In this work we considered core-corona form factor models to represent the structure of the block copolymer micelles. Analysis of SANS data without using a pre-selected model for the micelle structure is possible with, e.g., the generalized indirect Fourier transformation (GIFT) method [34]. The GIFT method involves no assumption on the structure but is computationally involved compared to form factor models for which analytical expressions are available [15]. We selected form factor models because (i) explicit analytical expressions are available, (ii) the models capture and quantify an important feature of the block copolymer micelle structure, i.e., core-corona, and (iii) these models have been already shown suitable in describing the micelle structure of POE alkyl ether surfactants [11,13], POE-POP-POE block copolymers [19-21,25],

and poly(dimethylsiloxane)-graft-POE copolymers [15].

Three domains can be distinguished in the block copolymer micellar solution: (i) the micelle core with low scattering length density (SLD) (the micelle core consists of mainly the hydrogenous POP blocks of the POE-POP-POE block copolymer and only small or no amount of deuterated solvent), (ii) the micelle corona with intermediate SLD (the micelle corona consists of the hydrogenous POE-blocks of the block copolymer and deuterated solvent), and (iii) the deuterated solvent phase with high SLD [15,19-21]. The core-corona form factor is a function of the SLD contrast between these three domains.

For a core-corona monodisperse sphere the form factor is written [15,19-21,62]:

$$P(q) = (1/V_2) \{ V_1 (\rho_1 - \rho_2) [3 J(qR_1) / qR_1] + V_2 (\rho_2 - \rho_s) [3 J(qR_2) / qR_2] \}^2 \quad (2)$$

$$V_i = 4\pi R_i^3 / 3$$

For a core-corona oblate ellipse [62]:

$$P(q) = (1/V_2) \int_0^1 |F(q)|^2 d\mu \quad (3)$$

$$F(q) = \{ V_1 (\rho_1 - \rho_2) [3 J(u_1) / u_1] + V_2 (\rho_2 - \rho_s) [3 J(u_2) / u_2] \}$$

$$V_i = 4\pi R_{i,major}^2 R_{i,minor} / 3$$

$$u_i = q [R_{i,major}^2 (1 - \mu^2) + R_{i,minor}^2 \mu^2]^{1/2}$$

For a core-corona prolate ellipse [62]:

$$P(q) = (1/V_2) \int_0^1 |F(q)|^2 d\mu \quad (4)$$

$$F(q) = \{ V_1 (\rho_1 - \rho_2) [3 J_1(u_1) / u_1] + V_2 (\rho_2 - \rho_s) [3 J_1(u_2) / u_2] \}$$

$$V_i = 4\pi R_{i,major} R_{i,minor}^2 / 3$$

$$u_i = q [R_{i,major}^2 \mu^2 + R_{i,minor}^2 (1 - \mu^2)]^{1/2}$$

where R_1 and R_2 are the radii of the micelle core and whole micelle (core+corona) respectively; the suffixes “major” and “minor” indicate the radii on the major axis and minor axis of the ellipse, respectively; ρ_1 , ρ_2 , and ρ_s are the SLDs of the core, corona, and solvent domains respectively; μ is the cosine of the angle between the scattering vector q and the direction of the major axis; and $J_1(x)$ is the first-order spherical Bessel function:

$$J_1(x) = [\sin(x) - x \cos(x)] / x^2 \quad (5)$$

For treating polydispersed systems, $P(q)$ must be averaged over the particle size distribution. The form factor for polydispersed spherical particles with a constant corona thickness (δ) is [62]:

$$P(q) = (1 / \langle V \rangle) \int_0^\infty G(R_1) F^2(qR_1) dR_1 \quad (6)$$

$$F(qR_1) = (4\pi/q^3) (\rho_2 - \rho_1) \{ \gamma J(qR_1 + q\delta) - J(qR_1) \}$$

$$J(x) = \sin(x) - x \cos(x)$$

$$\gamma = (\rho_s - \rho_2) / (\rho_1 - \rho_2)$$

$$G(R_1) = \{ R_1^Z / \Gamma(Z + 1) \} \{ (Z + 1) / \langle R_1 \rangle \}^{Z+1} \exp[-R_1 (Z + 1) / \langle R_1 \rangle]$$

$$Z = (1 / p^2) - 1$$

$$\langle V \rangle = 4\pi \langle R_1^3 \rangle / 3$$

$$\langle R_1^3 \rangle = \{ (Z + 3) (Z + 2) \langle R_1 \rangle / (Z + 1)^2 \}$$

where p denotes the polydispersity.

Under the assumption that the micellar solution consists of three regions and that there are only POP blocks in the micelle core and only POE blocks in the corona (this assumption is not severe since the SLD of POE and POP are similar relative to that of deuterium oxide (ρ_{D_2O})), the SLD values of the micelle core and corona, ρ_1 and ρ_2 , are given as a function of the volume

fraction of POP in the core (α_1) and the volume fraction of POE in the corona (α_2):

$$\rho_1 = \alpha_1 \rho_{\text{POP}} + (1 - \alpha_1) \rho_s \quad (7)$$

$$\rho_2 = \alpha_2 \rho_{\text{POE}} + (1 - \alpha_2) \rho_s$$

where $\rho_{\text{POP}} (= 0.325 \times 10^{10} \text{ cm}^{-2})$ and $\rho_{\text{POE}} (= 0.547 \times 10^{10} \text{ cm}^{-2})$ are the SLD values of POP and POE respectively [19]. α_1 and α_2 are functions of the micelle core and whole micelle radii, and the micelle association number ($N_{\text{association}}$), i.e., the number of amphiphiles per micelle:

$$\alpha_1 = N_{\text{association}} V_{\text{POP}} / V_{\text{core}} \quad (8)$$

$$\alpha_2 = N_{\text{association}} V_{\text{POE}} / (V_{\text{micelle}} - V_{\text{core}})$$

where $V_{\text{POP}} (= 5530 \text{ \AA}^3)$ [19], $V_{\text{POE}} (= 5410 \text{ \AA}^3)$ [19], V_{core} , and V_{micelle} are the volumes of the POP block, the POE blocks of a block copolymer molecule, the micelle core, and the whole micelle, respectively.

The solvent SLD (ρ_s) is expressed as:

$$\rho_s = \phi_{\text{D2O}} \rho_{\text{D2O}} + \phi_{\text{H2O}} \rho_{\text{H2O}} + \phi_{\text{Glucose}} \rho_{\text{Glucose}} \quad (9)$$

where ϕ_{D2O} , ϕ_{H2O} , and ϕ_{Glucose} are the volume fractions of deuterium oxide, hydrogenous water, and glucose in the solvent respectively, and $\rho_{\text{D2O}} (= 6.48 \times 10^{10} \text{ cm}^{-2})$ [19], $\rho_{\text{H2O}} (= -0.56 \times 10^{10} \text{ cm}^{-2})$ [19], and $\rho_{\text{Glucose}} (= 1.47 \times 10^{10} \text{ cm}^{-2}$, estimated value) [62] are the SLD values of deuterium oxide, hydrogenous water, and glucose respectively. Recall that the hydrogenous water originates from glucose monohydrate (thus the ratio of ϕ_{Glucose} and ϕ_{H2O} is fixed.)

The hard-sphere interaction structure factor (derived using the classical Ornstein-Zernike approximation for the spatial correlation fluctuations and the Percus-Yevick approximation for describing the direct correlation between two scattering objects with hard-sphere nearest-neighbor interacting potential) was used to describe interactions between

micelles [20,24,62]:

$$S(q) = 1 / [1 + 24 \phi G(2qR_{hs}) / (2qR_{hs})] \quad (10)$$

where ϕ is the micellar volume fraction, R_{hs} is the hard-sphere interaction distance, and G is a trigonometric function of $A = qR_{hs}$ and ϕ :

$$G(A) = \alpha (\sin(A) - A \cos(A)) / A^2 + \beta [2A \sin(A) + (2 - A) \cos(A) - 2] / A^3 + \gamma [-A^4 \cos(A) + 4\{(3A^3 - 6) \cos(A) + (A^3 - 6A) \sin(A) + 6\}] / A^5 \quad (11)$$

where α , β , and γ are

$$\alpha = (1 + 2\phi)^2 / (1 - \phi)^4 \quad (12)$$

$$\beta = -6\phi (1 + \phi / 2)^2 / (1 - \phi)^4$$

$$\gamma = (\phi / 2) (1 + 2\phi)^2 / (1 - \phi)^4$$

Note that ϕ is a function of the block copolymer concentration (C) and the polymer volume fraction in the micelle core (α_1) and corona (α_2), which, in turn, are functions of the form factor fitting parameters, radii of micelle core and micelle, and micelle association number ($N_{\text{association}}$):

$$\phi = C [V_{\text{POP}} / \alpha_1 + V_{\text{POE}} / \alpha_2] / (V_{\text{POP}} + V_{\text{POE}}) \quad (13)$$

Comparison between different models used to fit SANS data

In this section we discuss the selection of an appropriate model that we will utilize to extract structural information for the block copolymer micelles. We used the same model to analyze all the SANS data reported here. Figure 7 shows fitting curves originating from the combination of each of the four different form factors described in the previous section (monodisperse core-corona sphere, polydispersed core-corona sphere, monodisperse core-corona oblate (disk-like) ellipse, and core-corona prolate (cigar-like) ellipse) and the hard sphere interaction structure factor [62] to a representative SANS scattering pattern of the system EO₃₇PO₅₈EO₃₇ (8 wt%) - glucose monohydrate (40 wt%) - water (52 wt%) at 55 °C.

The monodisperse core-corona sphere form factor plus hard sphere interaction structure factor model (CSS_HS) has six fitting parameters (ϕ , ρ_1 , ρ_2 , ρ_s , R_1 , and $(R_2 - R_1)$) but among them only four fitting parameters are independent (because of equations (7) - (9)). The polydisperse core-corona spherical form factor plus hard sphere interaction structure factor model (PCF_HS) has seven fitting parameters, out of which five are “free”: ϕ , ρ_1 , ρ_2 , ρ_s , R_1 , $(R_2 - R_1)$ and p (polydispersity). The core-corona oblate (disk-like) or core-corona prolate (cigar-like) form factor plus hard sphere interaction structure factor models (OEF_HS or PEF_HS) have eight fitting parameters but six “free” parameters: ϕ , $(\rho_1 - \rho_2)$, $(\rho_2 - \rho_s)$, $R_{1\text{major}}$, $R_{1\text{minor}}$, $R_{2\text{major}}$, and $R_{2\text{minor}}$.

Different sets of fitting parameters can lead to curves that follow the SANS data. But many of these sets of parameters do not have physicochemical meaning. When using the core-corona model, our criterion has been to obtain sets of parameters that provide consistent α_2 and $N_{\text{association}}$ values as derived from equations (7), (8), and (13). We also considered (i) the micelle core to consist of only polymer and no solvent or solute, i.e., $\alpha_1 = 1$ [19,26,53], and (ii) the micelle corona to consist of polymer and water (deuterium oxide and hydrogenous water) but no solute (glucose). Thus we decrease the number of “free” parameters by two. From the sets of parameters which fitted well the SANS data, the obtained α_2 and $N_{\text{association}}$ values are consistent with $\pm 10\%$. These uncertainties are shown in the Figures 3 - 5 in the form of error bars.

From Figure 7, it becomes evident that the monodisperse core-corona prolate (cigar-like) ellipsoid form factor or the polydispersed core-corona spherical form factor used together with the hard sphere interaction structure factor (PCF_HS or PEF_HS) provide better fits than the other models considered here. The core-corona prolate (cigar-like) ellipsoid form factor is actually preferable (to the polydispersed sphere), because it enables a meaningful and

consistent interpretation on the experimental data. In particular, a change of polydispersity would not explain the observed changes in solution viscosity. Moreover, the polydispersity values obtained from fitting the PEF_HS model to the SANS data increase with increasing temperature. This trend is counterintuitive, given the results obtained previously by light scattering experiments [63].

As for assumption (i), it is appropriate for the experimental conditions (30 – 60 °C) that we used: the α_1 values of micelles formed by 8 wt% EO₃₇PO₅₈EO₃₇ in water were found 1 in the temperature range 30 - 60 °C [19]. Also the α_1 values of micelles formed by Pluronic P84 (EO₁₉PO₄₃EO₁₉) and P104 (EO₂₇PO₆₁EO₂₇) in water have been shown close to 1, i.e., 0.92 - 0.97 at temperatures 40 - 55 °C [26], and IR spectra have showed that the degree of hydration of POP of 10 wt% EO₃₇PO₅₈EO₃₇ in water decreased significantly above 25 °C [53].

In order to validate assumption (ii), SANS data fitting was carried out by applying the core-corona prolate (cigar-like) form factor and hard sphere interaction structure factor model (PEF_HS) and varying only x (the volume fraction of glucose monohydrate in the hydrated micelle corona) from $x=0.10$ to 0. The fits improve with decreasing x until $x=0$. This suggests that no or very little glucose exists in the micelle corona, thus validating assumption (ii) [48].

On the basis of all the above considerations, we have selected the monodisperse core-corona prolate (cigar-like) ellipsoid form factor and hard sphere interaction structure factor model (PEF_HS) to fit all SANS data (representative fits are shown in Figure 8) and extract the relevant structural parameters discussed in this paper. We note that in binary EO₃₇PO₅₈EO₃₇ - water solutions, the CSS_HS model fitted the SANS data slightly better than PEF_HS, but we still selected the PEF_HS model to fit these SANS data for easy comparison between micelles in the presence and absence of glucose.

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Figure 1. Temperature - concentration phase diagram for the micellization of Pluronic P105 ((EO)₃₇(PO)₅₈(EO)₃₇) in aqueous glucose solutions.

Figure 2. (a) Relative viscosity of aqueous $\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$ (Pluronic P105) solutions. (b) Relative neutron scattering intensity at $0.02225 \text{ \AA}^{-1}$ of the same solutions (the intensities are normalized with respect to those observed at 40 $^{\circ}\text{C}$). The arrows point out the onset of the micelle shape transition.

Figure 3. Variation of the micelle association number with temperature in the absence and in the presence of glucose.

Figure 4. Temperature and (block copolymer, glucose) concentration dependence of (a) micelle major radius, (b) micelle core major radius, (c) micelle minor radius, (d) micelle core minor radius, and major/minor radius ratio of (e) micelle and (f) micelle core.

Figure 5. Polymer volume fraction in the corona of the block copolymer micelle.

Figure 6. Schematic representation of micelle spacing in the solution, based on block copolymer micelle structural parameters obtained from SANS, and solvent volume per micelle and micelle number density estimated from these parameters.

Figure 7. Comparison between different models used to fit SANS data originating from Pluronic P105 (8 wt%) - glucose monohydrate (40 wt%) – water (52 wt%) solution at 55 °C. The models used are: core-corona sphere form factor (CSS_HS), polydispersed core-corona sphere form factor (PCF_HS), core-corona oblate (disk-like) ellipsoid form factor (OEF_HS) or core-corona prolate (cigar-like) ellipsoid form factor (PEF_HS) (see text for details). The hard sphere structure factor was used in all cases to account for intermicellar interactions.

Figure 8. SANS scattering patterns as a function of temperature. The lines indicate the fits of core-corona prolate (cigar-like) ellipsoid form factor and hard sphere interaction structure factor model (PEF_HS) to SANS data obtained from: (a) Pluronic P105 (8 wt%) - glucose monohydrate (40 wt%) – water solutions, and (b) Pluronic P105 (8 wt%) - water solutions.

Glucose-Induced Sphere to Ellipsoid Transition of Polyoxyethylene-Polyoxypropylene Block Copolymer Micelles in Aqueous Solutions

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