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Eduard Caicedo Casso

Jason E Bice

Lisa R. Nielsen

Jessica L Sargent

Seth Lindberg

See next page for additional authors

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Authors

Eduard Caicedo Casso, Jason E Bice, Lisa R. Nielsen, Jessica L Sargent, Seth Lindberg, and Kendra Erk

Rheo-Physical Characterization of Microstructure and Flow Behavior of Concentrated Surfactant Solutions

EDUARD A. CAICEDO-CASSO¹, JASON E. BICE¹⁺, LISA R. NIELSEN^{1^}, JESSICA L. SARGENT¹, SETH LINDBERG², AND KENDRA A. ERK^{1*}

¹ School of Materials Engineering, Purdue University, West Lafayette, IN 47907

² Corporate Engineering, The Procter & Gamble Company, West Chester, OH 45069

⁺ Current affiliation: Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115

[^] Current affiliation: Purdue University Graduate School, Office of Fellowships and Postdocs, Purdue University, West Lafayette, IN 47907

^{*} Corresponding author: erk@purdue.edu, 701 West Stadium Avenue, West Lafayette, IN 47907 USA, ORCID: 0000-0001-9238-1928

Abstract

Processing-relevant relationships between the microstructure and flow behavior of concentrated surfactant solutions were determined by a combination of basic rheological experiments, rheo-flow velocimetry tests, and flow birefringence measurements. The most common surfactant microstructures found in liquid soaps and other consumer care products – spherical, worm-like, and hexagonally packed micelles and lamellar structures – were recreated by varying the concentration of sodium laureth sulfate in water from 20 to 70 wt.% and adding salt in some cases. It was found that common features of flow curves, such as power-law shear thinning behavior, resulted from a wide variety of material responses including shear-induced wall-slip in micellar samples and plug flow in lamellar samples. Knowledge of key processing-structure-property relationships for concentrated solutions will allow engineers to develop more efficient industrial workflows for the scalable manufacturing of materials and feedstocks with reduced economic and environmental costs.

Introduction

There is a general trend for industries to create products with lower water footprints. (Koehler & Wildbolz, 2009) Using less water in every dose of liquid laundry detergent would save millions of

gallons of water every year. (Giagnorio et al., 2017) Concentrating detergents would also lead to reduced economic and environmental costs as fewer plastic bottles will be required, reducing waste, recycling, and transportation costs. (Saouter et al., 2001) In light of these potential savings, global consumer product companies are making public commitments to reduce the amount of water in their products. (R. Anderson, 2016)

However, concentrated materials are difficult to formulate and process using conventional production methods without increasing the input energy (cost) or altering the material's microstructure and thus its basic properties. For instance, as shown in Fig. 1, the microstructure of sodium laureth sulfate solutions – a widely utilized class of anionic surfactants – depends strongly on concentration. The molecules self-assemble into spherical micelles in the dilute state (often < 26 wt.%, depending on hydrophobic chain length) and form a solution that is optically isotropic and Newtonian. But in the concentrated state (typically > 26 wt.%), the molecules form optically birefringent, lyotropic crystalline structures with increased viscoelasticity and non-Newtonian character. (Roux et al., 1993) (Rosevear, 1968) (Laughlin, 1994) Additionally, formulation additives like oil or salt are known to alter the microstructure and bulk rheology of all phases (*e.g.*, induce cylindrical, “worm-like” micelles from spherical ones). (Laughlin, 1994)

Concentration	0-26%	26-60%	60-70%
Surfactant Phase	Spherical Micelles	Hexagonal	Lamellar
Polarized Light Micrograph
SLE ₁ S molecule

Fig. 1 Isotropic (22°C) phase diagram of solutions of sodium laureth sulfate (SLE₁S) in deionized water. SLE₁S has an average of twelve carbons in the hydrophobic tail and a single ethoxy group (n=1). Authors source

While the flow behavior of dilute surfactant solutions (spherical and worm-like micelles) has been studied for decades due to straightforward sample preparation and measurement, (Ezrahi et al., 2006) the characterization of concentrated surfactant solutions, including hexagonal and lyotropic structures, is inherently more challenging due to the complicated interplay between microstructure and shearing. (Berni et al., 2002) (Gentile et al., 2013) (Roux, 1993) (Richtering, 2001) Shear rheometry is usually a fast, reliable, and cost-effective technique to elucidate and measure the bulk viscosity and viscoelastic behavior of complex fluids for industrial applications. (Carreau, 2006) Engineers use rheometry measurements to solve day-to-day issues with fabrication or formulation of products. For instance, knowledge of a fluid's rheological response is required for the specification of pumps that transport liquids, often over distances of hundreds of meters and high flow rates, as well as for predicating residence times for the mixing of two slurries to achieve homogeneity. (Bird et al., 2007) (Kresta, 2003) Product designers rely on rheological information to ensure that final formulations have sufficient fluidity while dosing yet remain thick enough to perform adequately – *e.g.*, in the case of shampoo, the fluid should have sufficient viscoelasticity for it to remain in the consumer's hand after dosing without running through their fingers. Dilute detergents typically behave in a Newtonian manner and are thus easier to engineer and manufacture versus their complex, concentrated counterparts which are non-Newtonian and prone to structural changes under flow. (Kresta et al., 2004) (Basappa et al., 1999)

Despite the general utility of bulk shear rheometry, the routine data analysis associated with these measurements is typically “blind” to the formation and evolution of shear-induced flow instabilities within the sample. Shear rheometers calculate important rheological parameters based on assumptions such as the “no-slip” boundary condition, homogeneous laminar flow (simple shear) throughout the sample, and quiescent relaxation upon shear cessation. (Macosko, 1994) However, these assumptions are often violated during the study of complex fluids, as typical rheological responses of these materials often include a number of flow instabilities and artifacts, including signatures of wall-slip, shear banding, and fluid fracture. (Larson, 1992)

The root cause of instabilities in complex fluids varies widely, from edge effects (Hutton, 1969) (Archer et al., 1997) (Li & McKenna, 2015) and sample inhomogeneities (*e.g.*, trapped air bubbles and contaminants, segregation and sedimentation) (Husband et al., 1994) (Graham et al., 1998) to deformation-induced restructuring of the fluid driven by physical relaxation events, (Sui &

Mckenna, 2007) concentration gradients, (Veerman et al., 2005) and phase changes. (Rehage & Hoffmann, 1982) Wall-slip is considered to be a sudden disengagement of the bulk sample from the wall of the rheometer fixture, and as such, the wall-to-sample shear conditions differ from the bulk sample response. (Fardin, Divoux, et al., 2012) (Christel et al., 2012) (Malkin & Patlazhan, 2018) Shear banding is the formation of mesoscopic domains within the sample that display distinct deformation responses, typically manifest as domains with different local shear rates. (Fardin, Ober, et al., 2012) (Divoux et al., 2016) (Sprakel et al., 2008) Fluid fracture is an extreme example of strain localization within a sample, resulting in the creation of stationary domains (*i.e.*, zero or near-zero shear rate) adjacent to moving domains. (Ligoure & Mora, 2013) (Divoux et al., 2011b) (Hutton, 1963)

Indeed, the presence – known or unknown – of flow instabilities can create significant complications when interpreting rheological data. The unstable behavior, often transient in nature, coupled with the lack of physical, morphological feedback from standard rotational rheometers make these instruments prone to report artifacts and misleading data. For example, data which may at first glance appear to depict uniform shear thinning could actually result from the formation of localized shear bands and fracture zones within the specimen (*e.g.*, as observed with physically associating polymer solutions (Sprakel, 2008) (Erk et al., 2012) (Berret & Srro, 2001) (Berret et al., 2001)). This is especially true when attempting to measure fluids at processing-relevant shear rates that may exceed relaxation timescales of the fluid (*i.e.*, at moderate to high values of the Weissenberg number).

Therefore, to fully understand the rheological response of complex fluids for industrial applications – including the processing of concentrated surfactant solutions which are foundational to most consumer care products – it is essential to combine rheological characterization with suitable physical measurements. These so-called “rheo-physical” measurements are a group of hyphenated techniques that combine rheological measurements with microstructural, (Takeda et al., 2011) chemical, (Kotula et al., 2016) or physical evolution (Kiewiet et al., 2008) of soft materials and complex fluids. One broad class of rheo-physical measurements is typically referred to as rheo-flow velocimetry. (Markus et al., 2007) This is family of techniques in which local velocities within a sample can be directly quantified along with the simultaneously collection of rheological data. (Manneville et al., 2004) (Divoux et al., 2011a) (Herle et al., 2008) Rheo-flow

velocimetry techniques that involve rotational rheometers include, but are not limited to, magnetic resonance velocimetry (MRV), (Hanlon et al., 1998) (Poelma, 2017) particle image velocimetry (PIV), (Dimitriou et al., 2012) particle tracking velocimetry (PTV), (Thornell et al., 2016) laser doppler velocimetry (LDV), (Shapley et al., 2002) and ultrasonic speckle velocimetry (USV). (Manneville et al., 2007) The choice of technique for a given application is typically dictated by the material of interest; for instance, PIV, PTV, and USV systems may have similar spatial and temporal resolutions but USV systems will perform best for opaque samples while laser-based PIV and PTV systems are better suited for transparent or semi-transparent samples.

This study attempts to draw meaningful connections between the composition, microstructure, and rheological properties of solutions of sodium laureth sulfate (SLE₁S). A key objective of this study is to evaluate the quality of information about concentrated surfactants that can be obtained from a single flow curve, a basic rheological measurement of shear stress as a function of applied strain rate that is potentially ideal for screening a large number of different formulations in an industrial setting. SLE₁S was selected for use here to easily recreate the different microstructural arrangements that are most commonly found in the vast majority of consumer care products, from cleaning products to beauty care. The “model microstructures” – specifically, spherical micelles, worm-like micelles, hexagonally packed micelles, and lamellar structures – were created by simply varying the concentration of surfactant in water from 20 to 70 wt.% and by increasing the ionic concentration with the addition of salt (2-5% NaCl). X-ray scattering measurements were performed to characterize the microstructure of each solution, and for select samples, the evolution of the microstructure during shear deformation was directly observed through optical birefringence measurements in conjunction with a parallel-plate shear cell. Then a combination of basic shear rheometry and advanced rheo-physical measurements – rheometry coupled with ultrasound-based flow visualization – was performed to correlate rheometry data with the local deformation response of the solutions.

Materials and Methods

Materials

Sodium laureth sulfate (SLE₁S, where 1 denotes the presence of a single ethoxy group) surfactant paste was obtained from Stepan Company and used as received: STEOL CS170 UB SLE₁S, 70

wt.% surfactant in water, with a hydrophobic average chain length of 12 carbon (C) atoms and range of C10-C16. The raw SLE₁S paste will be denoted as “lamellar-70”, a naming convention adopted for this study that reports both the expected static microstructure of the sample and surfactant concentration. Reverse osmosis water was used to dilute the surfactant paste to concentrations of 40 wt.% and 20 wt.%, which will be denoted here as “hexagonal” and “spherical”, respectively. Surfactant and water were placed in sealed containers until complete dissolution and phase stabilization was achieved. The time scale for preparation of each sample varied from hours to several days depending on the final surfactant concentration. Sodium chloride (NaCl) was added to select samples to induce a microstructural rearrangement of the surfactant molecules: 2% NaCl was added to 20 wt.% solutions (creating the “worm-like” sample) and 5% NaCl was added to 40 wt.% solutions (creating the “lamellar-40” sample). The salt percentage was calculated over the total mass of surfactant and water mixture.

The USV measurements required the use of an ultrasonic contrast agent within each specimen. All specimens were seeded with hollow glass spheres (Sigma Aldrich) with a density of 1.1 g.cm⁻³ and an average diameter of 11 μm. Solutions containing 20 wt.% surfactant (*i.e.*, the spherical and worm-like micelle samples) were mixed with the glass spheres using a high shear mixer followed by a thermal equilibration. Other specimen (of hexagonal, lamellar-40, and lamellar-70 samples) were mixed with the glass spheres using a vacuum mixer to avoid air entrapment. Specimen volume for every USV measurement was approximately 25 cm³.

Basic Rheometry Measurements

An Anton Paar MCR 702 rotational rheometer coupled with a 10-mm Couette fixture was used to measure the shear stress and viscosity response of specimen of each surfactant solution. The shear stress and viscosity data were used to characterize the flow behavior of the different surfactant solutions as well as identify the critical shear rates for the onset of flow instabilities. Specimen volume was approximately 1.2 cm³. The application of shear followed a logarithmic ramp from the highest (100 s⁻¹) to lowest shear rates (0.001 s⁻¹). The parameters for data acquisition included strain control and steady state shear with 7 s of averaging per point.

Advanced Rheo-Flow Velocimetry Measurements

Ultrasonic speckle velocimetry (USV) is a measurement technique that uses a complex, high frequency backscattered signal to resolve the velocity and position of contrast agents within the volume of a deforming specimen, hence indirectly obtaining the one-dimensional velocity profile of the specimen. Local velocity measurements are achieved by using a high frequency ultrasonic transducer, complex electronic equipment to acquire and store the signal, and specialized software to process the stored data. The physical and electronic configuration of the USV system at Purdue University – constructed in collaboration with Sébastien Manneville following his pioneering design (Manneville, 2004) – allows for a spatial resolution of approximately 42 μm and temporal resolution of 0.1 s to 100 s. The minimum and maximum allowable shear rate are 0.2 s^{-1} and 200 s^{-1} , respectively. A brief overview of this technique is provided here; more in-depth description of this system is given elsewhere. (Manneville, 2004) (Bice, 2017)

The measurement process begins with the emission of an ultrasonic pulse and the reception of the respective echo. Pulses are generated with a user-defined pulse repetition frequency (PRF) that is selected based on the shear rate of the experiment – higher PRF values are required for high applied shear rates. Pulses and echoes exist in distinct times, allowing one ultrasonic transducer to perform as both emitter and receiver. Echoes are generated from the interaction between the ultrasonic pulses and contrast agents (here, 11 μm hollow glass spheres). During data post-processing, a cross-correlation algorithm uses two consecutive echoes to determine the delay time. The delay time between a pair of echoes and the geometrical constants of the physical hardware provide sufficient information to obtain the position within the rheometer gap and the radial velocity of a given contrast agent. Theoretically, only two pulses are needed to determine the velocity of an agent; however, in this experiment, 1,000 pulses divided into 1,000 segments are collected to provide statistical meaning to the calculated velocity values. Geometrical calibration of the hardware is achieved by using a Newtonian liquid, *e.g.*, reverse osmosis water seeded with contrast agents (see supplemental Fig. S1). The velocity of sound used in this experiment is obtained from separate time-of-flight measurements.

The USV system at Purdue University utilizes an ultrasonic transducer (Panametrics PI50-2-R0.50) with central frequency of 36 MHz and approximate focal length of 12.7 mm. The transducer is controlled by the following set of equipment: a function generator (BK precision 20GHz 4040-B); an Olympus pulser receiver (5073PR) that produces electrical signals at 220 V and gains

ranging between 0 to 40 dB; and a pre-amplifier (Olympus 5678) that amplifies the echo received by the ultrasonic transducer. A data acquisition PCI card (Agilent Digitizer U1084A) is used to convert the analog data into digital values, and custom MATLAB code is used for post-processing.

The USV system was used in combination with an Anton Paar MCR 302 rotational rheometer and custom-machined concentric cylinder cell, which included a 48-mm cylindrical rotor and surrounding semi-transparent cup, separated by a 0.83-mm gap and both precision machined from polymethyl methacrylate. To facilitate the motion of the ultrasound waves as well as ensure uniform temperatures within the specimen, the concentric cylinder cell and ultrasonic transducer were fully immersed in temperature-controlled water via a custom-built Plexiglas water chamber coupled with a JULABO water bath (designed and constructed in collaboration with Anton Paar; see supplemental Fig. S2). Unless specified, all measurements were conducted at 22°C.

To characterize the rheo-physical behavior of the different surfactant solutions, USV measurements were performed in conjunction with shear start-up tests, in which a constant shear rate is applied over time (see supplemental Fig. S3). For all samples and investigated shear rates, the velocimetry measurements were performed after the specimen had achieved steady state behavior. Shear rates of 0.7, 7, and 70 s⁻¹ were selected as good reference points to compare in every specimen. An exception was made for the hexagonal sample (40 wt.% surfactant, no added salt) which exceeded the torque limit of the rheometer; hence, only shear rates of 0.5 and 1 s⁻¹ were investigated for this specimen. A single specimen of each surfactant solution was used to evaluate the three different shear rates in descending order, and 30 s of pre-shear was applied before each measurement. Thus, for each specimen: 100 s⁻¹ pre-shear was applied before the 70 s⁻¹ shear start-up measurement; 10 s⁻¹ pre-shear was applied before the 7 s⁻¹ measurement; and 1 s⁻¹ pre-shear was applied before the 0.7 s⁻¹ measurement. The goal of the descending shear rate procedure and the application of pre-shear was to homogenize the specimen and to avoid transient, history-dependent effects during the measurements. Additionally, the velocimetry measurements for each specimen were acquired after 30 s of shearing to ensure steady state behavior was achieved.

In this study, velocimetry data are expressed as velocity, v , in mm.s⁻¹ as a function of gap length, x , in mm. The point $x = 0$ mm represents the position within the specimen directly adjacent to the rotor (*i.e.*, the moving wall) while $x = 0.83$ mm represents the position of the specimen adjacent to the stationary wall. Thus, for an ideal Newtonian specimen displaying uniform simple shear and

no wall-slip, $v(0)$ should equal the velocity of the moving wall (calculated as the applied shear rate multiplied by the gap length), $v(0.83 \text{ mm})$ should be zero, and all other $v(x)$ data (*i.e.*, local velocities within the volume of the specimen) will adopt a linear decay. Another illustrative plot used in this study is of the normalized velocity (v / v_0) as a function of normalized gap (x / x_0), where v_0 is the velocity of the moving wall and x_0 is the gap length (0.83 mm). Then, the resulting plot for an ideal Newtonian specimen will consist of data points organized along the line between point (0, 1) and (1, 0) and any deviation from linearity may indicate the presence of shear-induced flow instabilities within the volume of the specimen.

X-Ray Scattering Measurements

In this study, small-angle X-ray scattering (SAXS) measurements were performed to confirm that the surfactant solutions of interest contained the expected model microstructure. SAXS is a characterization technique that utilizes the scattering of an X-ray beam by electrons in a material to obtain averaged measurements of a material's structure and long-range nanoscale order. Depending on the density of the electron cloud and arrangement relative to neighboring species, a given molecule or molecular assembly will scatter X-rays at particular intensities and angles. Condensed assemblies such as surfactant micelles, with higher electron densities than the surrounding medium, would produce a unique scattering pattern indicating the average shape of the assemblies (*e.g.*, spherical or worm-like) and an average size parameter (*e.g.*, diameter or length). For repeating structures such as lyotropic organizations, multiple reflections will appear within the scattering pattern. The ratio of the scattering vector of higher order reflections to that of the primary reflection can be used to determine the nature of the repeat unit (*e.g.*, lamellar or hexagonal) and a domain size parameter (*e.g.*, center-to-center distance). A full explanation of this technique can be found elsewhere. (Feigin & Svergun, 1987)

All SAXS experiments were conducted using an Anton Paar SAXSpoint 2.0 system (note: this is a conventional SAXS machine that is *not* coupled with any rheometry systems). For each experiment, the specimen was placed in a paste cell containing Kapton windows and sealed with rubber O-rings to withstand vacuum pressure. The specimen was placed in the sample chamber, and the chamber was evacuated to a pressure below 1 mbar to minimize atmospheric scattering of the X-ray beam. Data for all samples was collected at a sample-to-detector distance (SDD) of 363 mm using an incident X-ray beam of 50.047 keV and 0.999 mA with a wavelength of 1.54 Å. For

each specimen, three frames of 300 s exposures were collected and averaged. Intensity values are reported in arbitrary units.

Two-dimensional data was reduced to one-dimensional curves using SAXS analysis software (Anton Paar), and further processing of one-dimensional data was completed using the IgorPro software (WaveMetrics) with Irena and Nika macros (Jan Ilavsky). Scattering vector values were determined from peak values after smoothing was applied in IgorPro to reduce the number of data points and produce more defined maximum values.

Optical Microscopy and Flow Birefringence Measurements

Optical microscopy under flow was conducted on specimens of the worm-like and lamellar-70 samples using a CSS450 optical shear stage (Linkam Scientific, Tadworth UK). This is a parallel plate cell with glass plates and a viewing window located at 7.5 mm off center; the gap and rotational velocity are electronically controlled. The vertical gap was set to 100 μm , and temperature maintained at 25°C. The stage was mounted on a Motic upright microscope (BA410E) fitted with 5x LM Plan lens (NA 0.13) and 20x lens (NA 0.4). Crossed polarizers above and below the stage were placed at 45° with respect to the flow across the window, such that optical retardance with the flow direction was maximized. Images were acquired using a QICam Fast 1394, color 12-bit camera controlled by Metamorph 7.7 software (Molecular Devices). Exposure times varied from 25 ms (for lamellar samples) and 150 ms (for worm-like samples). For flow birefringence measurements, the mean intensity across the field of view was tracked per frame during time-lapse acquisition. Specimens were tested immediately after preparation. Static polarized light imaging was achieved with the same software and camera equipped to a Zeiss Axioskop microscope with Plan NEOFLUAR Pol 10x (0.50NA) and 20x (0.30NA) objective lenses and 0.9NA condenser lens.

Results

Scattering Behavior

Fig. 2 Small-angle X-ray scattering patterns for the surfactant solutions: (a) 20 wt.% SLE₁S with 0% NaCl (spherical micelle sample) and 20 wt.% SLE₁S with 2% NaCl (worm-like micelle sample); (b) 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample) and 70 wt.% SLE₁S (lamellar-70 sample); (c) 40 wt.% SLE₁S (hexagonal sample)

Fig. 2 shows the SAXS patterns that were obtained for all surfactant solutions. Specimens from the 20 wt.% surfactant solutions without and with salt (Fig. 2a) displayed a broad reflection at $q = 0.1635 \text{ \AA}^{-1}$ and $q = 0.1414 \text{ \AA}^{-1}$, respectively. These reflections suggest the existence of spherical micelles that were polydisperse with an average diameter of $38.4 \text{ \AA}$, and the addition of salt to create the worm-like micelles increased the average size of these micelles to $44.4 \text{ \AA}$. Specimen of the 40 wt.% surfactant solution (Fig. 2c) displayed reflections at ratios of 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{12}$ times q^* , which is characteristic of a uniform hexagonally packed structure. (Manaia et al., 2017) The domain size parameter for this structure was calculated from q^* to be $d = 55.0 \text{ \AA}$. The 40 wt.% solution with 5 wt.% NaCl (Fig. 2b) displayed a shift from the hexagonally packed structure to a mixture of hexagonal and lamellar structures, the latter dominating the pattern. This is indicated by the reflections at ratios of 1, 2, and 3 times q^* , which are characteristic of a lamellar structure,

(Manaia, 2017) combined with continued contributions from the hexagonal structure at a reflection ratio of $\sqrt{12}$. The average domain size parameter for this specimen was calculated to be $d = 58.1$ Å. Specimen of the 70 wt.% surfactant solution (Fig. 2b) displayed distinct reflections at 1, 2, and 3 times q^* , indicating a uniform lamellar structure with a center-to-center distance between lamellae of 40.5 Å.

Basic Rheometry Results

Fig. 3 Flow curves for the surfactant solutions: 20 wt.% SLE₁S with 0% NaCl (spherical sample); 20 wt.% SLE₁S with 2% NaCl (worm-like sample); 40 wt.% SLE₁S (hexagonal sample); 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample); and 70 wt.% SLE₁S (lamellar-70 sample). The superimposed symbols represent the magnitudes of the shear stress plateaus observed from the flow-velocimetry shear start-up tests (see supplemental Fig. S3). For viscosity curves, see supplemental Fig. S4

Fig. 3 displays the stress response to increasing applied shear rates for all samples. The spherical sample behaved in a Newtonian manner, as the shear stress (τ) increased linearly with increasing shear rate ($\dot{\gamma}$) according to $[\tau = \eta\dot{\gamma}]$, with a viscosity value (η) of 6.1 mPa.s, roughly six times that of water. The behavior of the worm-like sample was shear rate dependent, with Newtonian behavior observed at < 5 s⁻¹ and shear thinning observed at greater rates, following a power-law $[\tau = k\dot{\gamma}^n]$ with index (n) of 0.14 and consistency (k) of 74 Pa.s (for reference see supplemental Fig. S5a).

The hexagonal sample displayed a strong shear thinning response over the full range of investigated shear rates. Two points of inflection were observed in Fig. 3, occurring at shear rates of $\sim 0.01 \text{ s}^{-1}$ and 10 s^{-1} . Qualitatively, the hexagonal sample exhibited behavior that was characteristic of a yield stress fluid with an apparent yield stress (τ_y) of 31 Pa. However, the behavior was not accurately captured by a Herschel-Bulkley fit, a model that is commonly used to describe yield stress fluids. (Divoux, 2011a) Instead, the shear stress response was better described using three different power laws at shear rate ranges of 0.001 to 0.01 s^{-1} , 0.01 to 10 s^{-1} , and 10 to 100 s^{-1} , with $n = 0.19, 0.41$, and 0.20 and $k = 115, 301, 480 \text{ Pa.s}$, respectively (for reference see supplemental Fig. S5b). Interestingly, although the rheometer data in Fig. 3 depicts the hexagonal sample as strongly shear thinning, this observation is inconsistent with actual observations—*e.g.*, it does not flow under gravity, and it fractures, slips, and squishes when touched.

While different in magnitude, the shear thinning responses of the lamellar-40 and lamellar-70 samples were best described using a Herschel-Bulkley model [$\tau = \tau_y + k\dot{\gamma}^n$] with $n = 0.54$, $k = 1.71 \text{ Pa.s}$, and $\tau_y = 0.29 \text{ Pa}$ for lamellar-40 and $n = 0.57$, $k = 8.9 \text{ Pa.s}$, and $\tau_y = 4.1 \text{ Pa}$ for lamellar-70. Both samples also displayed notable increases in the shear stress and viscosity data at the highest investigated shear rates (for reference see supplemental Fig. S5c).

Results from Advanced Rheo-Physical Measurements

To characterize the rheo-physical behavior of the different surfactant solutions, USV measurements were performed in conjunction with shear start-up tests at fixed shear rate values of $0.7, 7$, and 70 s^{-1} for the spherical, worm-like, and lamellar samples and 0.5 and 1 s^{-1} for the hexagonal sample. In general, there was good agreement between the steady state values of stress in the shear start-up tests and the associated values of stress in the flow curves (see Fig. 3).

Fig. 4 displays the rheo-flow velocimetry results for all surfactant solutions characterized using the USV system at Purdue. The spherical micelle sample (Fig. 4a) was the only sample that exhibited a velocity profile with nearly linear, simple shear behavior at all three investigated shear rates, as indicated by the good agreement of the data points with the dashed lines in the plot.

Fig. 4 Rheo-flow velocimetry results for three different applied shear rates, 70 s^{-1} (red circles), 7 s^{-1} (black diamonds), and 0.7 s^{-1} (blue squares), for the following surfactant solutions: (a) 20 wt.% SLE₁S with 0% NaCl (spherical sample); (b) 20 wt.% SLE₁S with 2% NaCl (worm-like sample); (d) 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample); and (e) 70 wt.% SLE₁S (lamellar-70 sample). For the (c) 40 wt.% SLE₁S (hexagonal sample), 0.5 s^{-1} (gray pentagrams) and 1 s^{-1} (brown hexagons) were the applied shear rates. In every plot, the dashed colored lines indicate the simple shear velocity profile expected for each applied shear rate

The worm-like micelle sample (Fig. 4b) exhibited simple flow characteristics at the lowest applied shear rate (0.7 s^{-1}). At the highest investigated shear rate of 70 s^{-1} , clear evidence of slip at the moving wall was observed as indicated by the reduced magnitude of the velocimetry data compared with the expected velocity profile.

The hexagonal sample (Fig. 4c) displayed evidence of strong wall-slip at both the moving and stationary walls of the rheometer fixture while maintaining a nearly constant velocity throughout its volume, thus adopting a velocity profile characteristic of plug flow. This plug flow response was observed for both values of applied shear rate.

The lamellar-40 sample (Fig. 4d) exhibited plug flow-like behavior, though not as idealized as the behavior displayed by the hexagonal sample as not all portions of the specimen volume deformed at a constant velocity (*e.g.*, the region near the stationary wall, $x \sim 0.6\text{-}0.8 \text{ mm}$). For the lamellar-40 sample, wall-slip was also observed. At 70 s^{-1} , evidence of a discontinuity was observed at $x \sim 0\text{-}0.8 \text{ mm}$, as neighboring velocimetry measurements reported very different values. Specifically, the velocimetry data representing a layer of solution $\sim 80 \text{ }\mu\text{m}$ in thickness near the moving wall was approximately 75% of the wall velocity but all data between $80\text{-}600 \text{ }\mu\text{m}$ was approximately 50% of the wall velocity.

The lamellar-70 sample (Fig. 4e) was perhaps the most interesting sample as the basic rheology was similar to the lamellar-40 sample (Fig. 4d) but with a strikingly different velocity profile at the highest shear rate. At low shear rates (0.7 and 7 s^{-1}), the lamellar-70 sample exhibited plug flow behavior with wall-slip at both the moving and stationary walls. However, at 70 s^{-1} , a behavior more like simple shear was observed and there was no evidence of a discontinuous velocity profile, such as the one observed in the lamellar-40 sample.

Polarized Light Imaging and Birefringence Monitoring

Light microscopy (crossed-polarized imaging) and flow birefringence was used to complete the structural characterization of the SLE₁S samples. Fig. 5 shows micrographs of expected microstructural phases under cross-polars to orient readers to the liquid crystalline patterns of common surfactant phases (Rosevear, 1954). Surfactant microstructures appeared bright or dark depending on how they were ordered with respect to the polarized illumination. The lamellar-70 sample prepared gently with minimal shear exhibited randomized domains of optically-isotropic,

dark sheets (see Fig. 5a, blue arrow) and optically anisotropic oily streaks that appeared bright (Fig. 5a, white arrow). Rolled-up sheets formed “onion”-like spheres consisting of concentric layers, called multilamellar vesicles (MLVs) which exhibit Maltese-cross patterns (Fig. 5b, white arrow) made here by dispersing SLE₁S in 1 Pa-s silicone oil. Shearing the lamellar 70 sample from Fig. 5a back and forth uniaxially while mounted on the microscope slide resulted in aligned oily streaks (Fig. 5c). The sheared lamellar-40 sample (Fig. 5d) displayed a lower concentration of oily streaks than the lamellar-70 sample (Fig. 5c) due to the differences in surfactant and salt concentrations. Lastly, the fan-like patterns of the hexagonal sample were visible after significant applied shear between the microscope slides (Fig. 5e).

Fig. 5 Light microscopy (crossed-polarized) of 70 wt.% SLE₁S (lamellar-70 sample) at rest (a); dispersed in silicone oil to demonstrate MLV patterns (b); and after shear (c); (d) 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample) after shear; (e) 40 wt.% SLE₁S (hexagonal sample) after shear

Fig. 6 is composed of time-lapsed snapshots of the microstructural evolution of the lamellar-70 sample at various, constant shear rates. The first image at time-zero, taken after sample loading but prior any applied shear, exhibited many liquid crystalline domains that were randomly oriented, so the image was relatively dark compared to subsequent ones (Fig. 6a). Oily streaks and some MLVs organized as 7 s^{-1} was applied for 3 minutes. As shown in Fig. 6b, higher shear rates

(70 s^{-1}) increased the rate of assembly, producing optically brighter oily streaks aligned with the flow direction (top to bottom). With increasing duration of shear, oily streaks became more and more organized with the flow. Finally, to test reversibility and relaxation rates, a final interval of low shear (7 s^{-1}) was applied (see Fig. 6c). The crystalline lamellar superstructures did not display strong evidence of relaxation or reorganization during experimental timescales (order of minutes).

Fig. 6 Polarized light imaging of 70 wt.% SLE₁S (lamellar-70 sample) in the Linkam shear stage illustrating shear-induced microstructural rearrangement during consecutive 3-minute intervals of rotation at (a) 7 s^{-1} , (b) 70 s^{-1} , and (c) 7 s^{-1} (note that direction of flow is from top to bottom in each image)

Discussion

As mentioned in the introduction, this study attempted to evaluate the quality of information about a model surfactant solution that was obtained from flow curve measurements. To conduct this evaluation, with a focus on potentially uncovering the solutions' true rheological responses and thus determining accurate structure-property relationships, connections were established between the shear rheometry data (Fig. 3), rheo-flow velocimetry data (Fig. 4), and flow-imaging results (Fig. 5 and 6), coupled with prior knowledge about surfactant solution formulation and phase behavior (Fig. 1).

Newtonian Behavior of the Spherical Micelle Sample

The sample containing 20 wt.% SLE₁S formed spherical micelles in solution as expected. The transformation into ordered structures of surfactant molecules was driven by the continuous battle between the entropy and enthalpy to lower the total energy of the system. (Israelachvili, 2011) The formation of micelles (spherical in this case) requires adequate amounts of surfactant and/or counterions (Lerouge & Berret, 2009); 20 wt.% surfactant in solution was expected to be enough to form spherical micelles because this concentration was far above the expected critical micelle concentration (0.023 wt.%). (Aoudia et al., 2010) SAXS results confirmed the presence of spherical micelles and did not show any evidence of long-range arrangement. Lacking long-range order, it was thus expected that the dilute solution of spherical micelles exhibited Newtonian behavior analogous to hard spheres in a sea of solvent. (Ezrahi, 2006) (Caicedo-Casso et al., 2018) (Larson, 1999) This expectation was consistent with the flow curves in Fig. 3 and velocity profiles in Fig. 4a – data which is replotted in Fig. 7 and normalized for direct comparison. The Newtonian, simple shear response was a consequence of the displaced volume of solvent that each sphere produced; that is, micelle-micelle interactions were negligible compared to the hydrodynamic drag that each micelle produced during deformation. (Panton, 2013) (Cassagnau, 2013) A deviation between the velocimetry data and expected simple shear response was observed at the lowest shear rate, most likely a consequence of slight fluctuations of the applied shear rate due to the finite torque sensitivity of the stress-controlled rheometer.

Fig. 7 Relationship between flow curve data from Fig. 3 and local velocity profiles at three shear rates from Fig. 4a for the 20 wt.% SLE₁S solution (spherical sample). Inset plots display the normalized velocity as a function of normalized gap

Bimodal Behavior of Worm-Like Micelle Sample

The worm-like micelle sample was created with addition of 2% NaCl to the 20 wt.% surfactant solution. The addition of counterions (*i.e.*, Na⁺) screened the anionic head groups of the surfactant molecules (Walker, 2001) so that the micelles transformed from spheres into elongated, cylindrical geometries. (Ezrahi, 2006) These worm-like micelles have remarkable structural stability as well as regenerative properties (*i.e.*, the ability to break and reform in solution) and are widely used in the lubricant, pharma, and personal and home care industries. (Walker, 2001) (Berret, 2006)

X-ray scattering and flow birefringence measurements were used to verify the microstructure of this sample at the Angstrom-level. SAXS characterization suggested a larger micelle diameter compared to the spherical sample and no long-range order. This implies that the worm-like micelles were isotropic and amorphously entangled at rest, and the measured micelle size indicated the average diameter of the worms. While it can be difficult to confirm the presence of cylindrical micelles using SAXS, the characteristic signatures of these structures have been observed during flow birefringence measurements at increasing applied shear rates – see supplemental Fig. S6. (Mishra et al., 1993) (Wunderlich et al., 1987)

Fig. 8 Relationship between flow curve data from Fig. 3 and local velocity profiles at three shear rates from Fig. 4b for the 20 wt.% SLE₁S and 2% NaCl (worm-like sample). Inset plots display the normalized velocity as a function of normalized gap

The flow curve of the worm-like sample displayed a Newtonian response at low shear rates and shear thinning behavior at higher rates, as previously reported by many others. (Walker, 2001) (Makhloufi et al., 1995) (Rogers et al., 2014) As expected, the Newtonian response corresponded with a simple shear velocity profile (see Fig. 8). Also shown in Fig. 8, at the approximate onset of shear thinning, slight wall-slip was observed which increased in magnitude at higher applied shear rates. Thus, the measured shear thinning response was not representative of the bulk sample but was instead a consequence of shear-induced wall-slip.

Usually, the bimodal rheology of samples containing worm-like micelles is attributed to the shear-induced formation of bands of different viscosities. (Fardin, 2012) (Makhloufi, 1995) (Mohammadigoushki & Muller, 2016) However, velocimetry results did not show strong evidence of shear band formation, which is typically manifest as a “kink” (change of slope) in the velocity profile. Some have found that the formation of shear bands can be delayed or even prevented if wall-slip is present. (Lettinga & Manneville, 2009) Thus, as shear bands were not observed here, their formation was most likely prevented by the slippage that occurred at medium (7 s^{-1}) and high shear rates (70 s^{-1}). From a molecular viewpoint, if the adhesive forces between the solution and

fixture walls are weaker than the cohesive forces within the solution, stress will be relaxed (deformation energy released) by the formation of a zone of high shear at the solution-wall interface – *i.e.*, the occurrence of wall-slip will reduce the likelihood (and energetic driving force) for other flow instabilities to nucleate. (Erk, 2012) (Lettinga, 2009)

Plug Flow of the Hexagonal Sample

The increased surfactant concentration produced a transition from dense spherical micelles at 20 wt.% to a hexagonal organization of elongated cylindrical micelles at 40 wt.%. (Montalvo et al., 1996) The flow curve response of the hexagonal sample was shear thinning over all investigated shear rates, consistent with previous studies. (Montalvo, 1996) (Sushko et al., 2002) However, signatures of plug flow were observed in the rheo-flow velocimetry results (see Fig. 9). Thus, the sheared hexagonal sample was not uniformly shear thinning through its volume. Instead, deformation appeared to be localized to regions of the solution that were directly adjacent to the moving and stationary walls. These shear thinning “lubrication layers”, as they are sometimes called, (Manneville, 2004) (Murray et al., 2018) facilitated the motion of the bulk plug of solution.

Compared to disordered cylindrical micelles and lamellar phases, others have shown that the hexagonal phase of surfactant solutions typically exhibits greater viscoelasticity due to increased interactions between neighboring micelles in the hexagonally packed microstructure. (Sushko, 2002) So even though it cannot be directly measured here, the plug of solution was assumed to have a rheological response similar to a viscoelastic solid based on observations of the solution during sample preparation. What was detected in the basic rheometry experiments was the shear thinning response of the lubrication layers that effectively surround the viscoelastic plug within the solution. And while velocimetry measurements were not possible within these layers due to the 42- μm spatial resolution of the USV system, here an attempt is made to explain the molecular-level mechanisms that are responsible for the shear thinning behavior observed in the flow curve based entirely on the known microstructure of the sample, *i.e.*, hexagonally close packed cylindrical micelles.

Fig. 9 Relationship between flow curve data from Fig. 3 and local velocity profiles at three shear rates from Fig. 4c for the 40 wt.% SLE₁S (hexagonal sample). Inset plots display the normalized velocity as a function of normalized gap

Deformation of a hexagonal phase is the result of cooperative and associative movement of small elastic units (*i.e.*, solid-like domains). (Sushko, 2002) (Ahir et al., 2002) Hexagonal domains do not have a mesoscopic uniform orientation; thus, each domain requires a specific level of energy to move and rotate before it completely aligns in the direction of the flow, contributing to a mesoscopic-type movement. Therefore, critical shear rates can produce movement of specific domains, *e.g.*, those in contact with the fixture walls, which lead to the creation of a transient, friction-reducing lubricating layer. Once the lubrication layers are created, the viscoelastic plug effectively disengages from the moving wall and acquires a lower flow velocity. This behavior will persist until a critical level of strain is surpassed, generating an effective orientation of an adjacent layer of hexagonal domains. (Sushko, 2002) These critical strain values required for mesoscopic movement may explain the different power laws observed in the flow curve of hexagonal sample. And as more hexagonal domains in the lubrication layer align in the flow direction, less torque is required to achieve the same applied shear rate, yielding a shear thinning response.

Apparent Yield Stresses of Lamellar Samples

In the context of this study, lamellar-40 and lamellar-70 samples were designed to be model concentrated surfactant solutions that behave as yield stress fluids. (Ahmed Siddig et al., 2006) Both samples displayed similar rheology and Angstrom-scale microstructure and were described by the Hershel and Bulkley model with different yield stresses: 0.29 Pa for lamellar-40 and 4.1 Pa for lamellar-70. Yield stress is defined as the transition (critical or transient) from a solid-like to liquid-like state of deformation of a complex fluid. (Divoux, 2011a) However, accurately quantifying yield stress using a shear rheometer can be quite complex as contributions from different flow behaviors, including wall-slip and shear banding, can create artifacts impacting the measurement of this parameter. (Bonn & Denn, 2009) Evidence of such artifacts are seen by directly comparing the flow curve and velocimetry data, displayed in Fig. 10 and 11.

The lamellar-40 sample (Fig. 10) exhibited plug flow at every applied shear rate (0.7 s^{-1} , 7 s^{-1} and 70 s^{-1}). The highest shear rate resulted in the formation of a discontinuity near the moving wall and small shear band near the stationary wall ($x / x_o > 0.8$). The lamellar-70 sample (Fig. 11) displayed plug flow at low shear rates, the formation of a slight shear band near the moving wall ($x / x_o < 0.2$) at intermediate shear rates, and evidence of a possible “recovery” of simple shear behavior at high shear rates. Thus, due to the occurrence of plug flow and some areas of shear banding in the velocimetry data, the flow curve data for these lamellar samples should not be used to directly quantify a “true” (bulk) yield stress value, as such values seem to represent only the stress required to deform a relatively small volume of sample, *i.e.*, lubrication layers around the plug.

Fig. 10 Relationship between flow curve data from Fig. 3 and local velocity profiles at three shear rates from Fig. 4d for the 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample). Inset plots display the normalized velocity as a function of normalized gap

Fig. 11 Relationship between flow curve data from Fig. 3 and local velocity profiles at three shear rates from Fig. 4e for the 70 wt.% SLE₁S (lamellar-70 sample). Inset plots display the normalized velocity as a function of normalized gap

The mechanics of plug flow within the lamellar samples is believed to be similar to the hexagonal sample in which lubrication layers are created by the rearrangement and flow of small, solid-like domains composed of hexagonally packed cylindrical micelles. For the lamellar samples, domains are most likely composed of sheets and oily streaks, which are not expected to be as elastic as the hexagonal domains. This most likely explains why deformation occurred at relatively lower values of stress for the lamellar samples compared with the hexagonal sample (see flow curve in Fig. 3). (Briceño-Aumada et al., 2016) (Panizza et al., 1998) (Gentile et al., 2012)

To fully understand the flow behavior of the lamellar samples, it is also necessary to consider the shear history dependency of the lamellae in the microstructure. It is well known that a lamellar phase under continuous and steady shear (flow or oscillatory) undergoes a series of microstructural rearrangements due to their nonequilibrium nature. (Fritz et al., 2003) As shown in the flow

birefringent images of Fig. 6 for the lamellar-70 sample, the organization of oily streaks varied over a short period of time from random orientation at rest to highly oriented at high shear rates and this rearrangement appeared to be non-reversible. Thus, the oriented oily streaks most likely dominated the lamellar microstructure that existed during the flow curve and flow velocimetry measurements, which were conducted from high to low applied shear rates. Therefore, the differences in the measured flow behavior of the lamellar-70 and lamellar-40 samples were most likely dependent on the organization of oily streaks, as described below.

Comparing Fig. 10 and 11, the lamellar-40 sample displayed plug flow at the highest applied shear rate while the lamellar-70 sample displayed behavior approaching simple shear. This difference was most likely a function of the lamellar spacing in the two samples, a direct result of the differences in surfactant concentration (70 wt.% vs. 40 wt.%) and ionic strength (0% NaCl vs. 5% NaCl). (Gentile, 2013) (Diat et al., 1995) The lamellar spacing does not change with the formation of MLV; however, domains of MLV lead to the formation of continuous oily streaks which change the viscosity behavior of lamellar phase. (Fritz, 2003) As shown in Fig. 5, oily streaks were observed to be nearly adjacent in the lamellar-70 sample while the lamellar-40 sample contained streaks that were separated by ~ 50 microns. This increased spacing (reduced concentration) of oily streaks in the lamellar-40 sample most likely increased the likelihood of strain localization at high shear rates (manifest as lubrication layers and plug flow) while the concentrated structure of the lamellar-70 sample displayed a more uniform deformation response at high shear rates (manifest as simple shear).

Summary and Implications

This study demonstrates a potential workflow to determine the processing-relevant relationships between the microstructure and flow behavior of concentrated surfactant solutions using a combination of basic rheological experiments, rheo-flow velocimetry tests, and flow birefringence measurements. A key objective was to evaluate the quality of information about a liquid surfactant that was obtained from a flow curve experiment performed in a shear rheometer. It was found that common features of flow curves (*e.g.*, power-law shear thinning behavior) can result from a wide variety of material responses, including shear-induced wall-slip and plug flow, and rheo-physical experiments were required to correlate the local deformation behavior with its rheological signature.

The most dilute surfactant solution (20 wt.% SLE₁S) formed disordered spherical micelles and displayed Newtonian, simple shear behavior. When salt was added to the solution, worm-like micelles formed and displayed wall-slip at shear rates corresponding to shear thinning behavior in the flow curve. When the surfactant concentration was increased to 40 wt.% SLE₁S, the solution became a viscoelastic solid-like material with a microstructure of hexagonally packed cylindrical micelles. When shear deformation was applied, plug flow was observed at shear rates which corresponded to shear thinning in the flow curve, a response most likely generated by a lubrication layer of aligned cylinders surrounding the viscoelastic plug. Upon the addition of salt, the microstructure was transformed to a lamellar structure, which also displayed shear thinning plug flow at all investigated shear rates. At the highest surfactant concentration of this study (70 wt.% SLE₁S), a lamellar microstructure was present and behaved similarly to the less concentrated lamellar sample except that at very high shear rates, the viscosity slightly increased and behavior approaching simple shear was observed.

Future work can expand from this study to include other formulation and processing-relevant parameters such as temperature and salt content. The timescales of microstructural reorganization during or following shear deformation could also be characterized in more detail to provide additional insight into some of the critical shear rates observed here in an effort to further define the relationships between processing, microstructure, flow properties, and performance.

In general, the shear-induced microstructures of concentrated surfactant solutions, which form the chemical base for many detergents and personal care products, can have very different rheological properties ranging from strongly thixotropic phases to phases that are shear thinning. When concentrated solutions are exposed to high shear forces, a variety of behaviors can occur, such as shear banding, fluid fracture, and wall-slip. While these are typically assumed to be bad for industrial processing (*e.g.*, resulting in material inhomogeneity), it is largely unknown if these behaviors could potentially enhance the manufacturing of concentrated materials, perhaps by reducing the pressures needed to pump fluids through a pipe or by controllably mixing multi-phase components during pumping.

In light of the recent sustainability challenges to create more concentrated products, company resources are most often devoted to new capital manufacturing equipment, and few (if any) resources are devoted to developing a better understanding of the processing science related to

more complex, concentrated raw materials and feedstocks. Until the fundamental scientific relationships between microstructure, properties, and large-scale processability and performance are better defined for concentrated complex fluids, industry will continue to sacrifice valuable resources to inefficient and unsustainable manufacturing processes.

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Supplemental Material

Fig. S1 Flow-velocimetry calibration curves expressed as (a) velocity in mm.s^{-1} versus gap in mm; (b) normalized velocity versus normalized gap (refer to “Advanced Rheo-Flow Velocimetry Measurements” section in manuscript). The calibration was performed at shear rates of 4 s^{-1} , 10 s^{-1} , 15 s^{-1} , 20 s^{-1} and 30 s^{-1} . The uncertainty of measured experimental velocity versus the expected velocity is $\pm 0.18 \text{ mm.s}^{-1}$. The colored dashed lines in (a) and solid black line in (b) indicate the simple shear velocity profile expected for each applied shear rate

Fig. S2 Schematic of the flow-velocimetry system that was created at Purdue University through collaboration with Prof. Sébastien Manneville (Laboratoire de Physique, Ecole Normale

Supérieure de Lyon, France) and with support from Anton Paar and Procter & Gamble. Additional details can be found in Bice, J. E. (2017). *Using Ultrasonic Speckle Velocimetry to Detect Fluid Instabilities in a Surfactant Solution* (Master Thesis Purdue University). Retrieved from ProQuest Dissertations Publishing (10684303)

Fig. S3 Flow-velocimetry shear start-up data for the following specimens of surfactant solutions: 20 wt.% SLE₁S with 0% NaCl (spherical sample); 20 wt.% SLE₁S with 2% NaCl (worm-like sample); 40 wt.% SLE₁S (hexagonal sample); 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample); and 70 wt.% SLE₁S (lamellar-70 sample). Shear stress response over time is presented in a log-log scale

Fig. S4 Viscosity curve for the surfactant solutions: 20 wt.% SLE₁S with 0% NaCl (spherical sample); 20 wt.% SLE₁S with 2% NaCl (worm-like sample); 40 wt.% SLE₁S (hexagonal sample); 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample); and 70 wt.% SLE₁S (lamellar-70 sample)

Fig. S5 Fits for the flow curves of (a) 20 wt.% SLE₁S with 0% NaCl (spherical sample) and 20 wt.% SLE₁S with 2% NaCl (worm-like sample); (b) 40 wt.% SLE₁S (hexagonal sample); (c) 40 wt.% SLE₁S with 5% NaCl (lamellar-40 sample) and 70 wt.% SLE₁S (lamellar-70 sample). The solid line represents the applied models (as described in the manuscript) and the semi-transparent symbols are the raw data points. The symbols in the equations stand for shear stress (τ), shear rate ($\dot{\gamma}$), power index (n), viscosity (η), yield stress (τ_y), and consistency (k). Origin 2018b linear and non-linear fitting tool was used

Fig. S6 Flow birefringence results for 20 wt.% SLE₁S with 2% NaCl (worm-like micelle sample), presented as relative mean intensity (i_{re}) versus applied shear rate. The relative mean intensity was used as an indicator of the degree of organization of the specimen. Higher mean intensity values correlate to a higher degree of organization or alignment resulting from the transient increase in birefringence. The onset shear rate is the intercept between the two power law fits. The onset shear rate proves the presence of cylindrical micelles as it represents the rate of deformation at which the worm-like sample transitioned from isotropic to highly aligned, producing a bright flash under crossed polarizers and the drastic change in the relative mean intensity. This onset shear rate was comparable to the shear rate at which shear thinning initiated in the measured flow curve (see Fig 3 in the main document)