Rheological characterizations of wormlike micellar solutions containing cationic surfactant and anionic hydrotropic salt
Ya Zhao, Simon J. Haward and Amy Q. Shen

Citation: Journal of Rheology 59, 1229 (2015); doi: 10.1122/1.4928454
View online: https://doi.org/10.1122/1.4928454
View Table of Contents: https://sor.scitation.org/toc/jor/59/5
Published by the The Society of Rheology

ARTICLES YOU MAY BE INTERESTED IN

Microstructure and shear rheology of entangled wormlike micelles in solution
Journal of Rheology 53, 441 (2009); https://doi.org/10.1122/1.3072077

Relaxation time of dilute polymer solutions: A microfluidic approach
Journal of Rheology 61, 327 (2017); https://doi.org/10.1122/1.4975933

The rheology and microstructure of branched micelles under shear
Journal of Rheology 59, 1299 (2015); https://doi.org/10.1122/1.4929486

Wormlike micellar solutions: II. Comparison between experimental data and scission model predictions
Journal of Rheology 54, 881 (2010); https://doi.org/10.1122/1.3439729

Determination of characteristic lengths and times for wormlike micelle solutions from rheology using a mesoscopic simulation method
Journal of Rheology 59, 903 (2015); https://doi.org/10.1122/1.4919403

Concentration, salt and temperature dependence of strain hardening of step shear in CTAB/NaSal surfactant solutions
Journal of Rheology 61, 967 (2017); https://doi.org/10.1122/1.4996008

True powder rheology
Find out more

Anton Paar
Rheological characterizations of wormlike micellar solutions containing cationic surfactant and anionic hydro tropic salt

Ya Zhao

Mechanical Engineering Department, University of Washington, Seattle, Washington 98195

Simon J. Haward

Micro/Bio/Nanofluidics Unit, Okinawa Institute of Science and Technology Graduate University, Onna, Okinawa, 904-0495, Japan

Amy Q. Shen\(^{a)}\)

Mechanical Engineering Department, University of Washington, Seattle, Washington 98195 and Micro/Bio/Nanofluidics Unit, Okinawa Institute of Science and Technology Graduate University, Onna, Okinawa, 904-0495, Japan

(Received 12 January 2015; final revision received 24 July 2015; published 24 August 2015)

Abstract

Aqueous micellar solutions of cationic surfactant cetyltrimethylammonium bromide (CTAB) and organic hydro tropic salt 3-hydroxy naphthalene-2-carboxylate (SHNC) in the semidilute regime have been characterized by linear and nonlinear rheology, and dynamic light scattering. The strong hydrophobicity and naphthalene structure present in the SHNC induces significant growth of CTAB wormlike micelles and promotes stable micellar network formation. Focusing primarily on 75 mM CTAB/SHNC solution, we correlate the rich rheological behavior with structural transitions of the micellar network under different deformation histories with temperatures in the range of 20°C < T < 40°C. Viscous dissipation dominates at low temperature, while short range interactions among micellar head groups, reorganization of micellar networks play important roles at higher temperatures, leading to complex stress responses under large deformations. The influence of double benzene rings on the response of transient and large amplitude oscillatory shear flows in the system was further elucidated by comparing the rheological behavior of CTAB/SHNC with CTAB/NaSal at the same salt and surfactant concentrations. Our studies distinguished SHNC as a stable hydro trope in a semidilute cationic surfactant system under thermal variations, with potential applications such as drag reduction and fracturing fluids in oil recovery. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1122/1.4928454]

\(^{a)}\)Author to whom correspondence should be addressed; electronic mail: amy.shen@oist.jp

© Author(s) 2015

J. Rheol. 59(5), 1229-1259 September/October (2015) 0148-6055/2015/59(5)/1229/31 1229
I. INTRODUCTION

An amphiphilic surfactant molecule consists of a hydrophilic head-group covalently bonded to one or more hydrophobic tails. In aqueous solvents, above the critical micelle concentration (CMC), noncovalent interactions drive the self-assembly of amphiphiles into supramolecular nanostructures in which tails are isolated from water and head groups are optimally spaced. These structures include spherical and wormlike micelles, vesicles, bilayers, and various other morphologies [Israelachvili (1985)]. Mixing ionic surfactants with inorganic or organic salts, such as sodium chloride (NaCl), sodium salicylate (NaSal), or 3-hydroxy-naphthalene-2-carboxylate (SHNC), the electrostatic repulsion between the charged head groups is screened by oppositely charged counterions. This can consequently change the micelle packing parameters in the surfactant system, with the formation of rod-like micelles becoming more energetically favorable [Abdel-Rahem (2008); Brackman and Engberts (1991); Hassan et al. (1996), Israelachvili (1985); Kim and Yang (2000); Oelschlaeger et al. (2010, 2003); Ohlendorf (1986)]. Hydrotropic salts are a class of amphiphilic compounds that cannot form micellar aggregates, but can solubilize organic molecules in water. Structurally similar to surfactants, hydrotropic salts can act as strong “binding” additives and reduce surface tension in an aqueous solution. A number of organic hydrotropic salts such as NaSal [Rehage and Hoffmann (1988a); Shikata et al. (1987)], SHNC [Mendes et al. (1997, 1998)], p-toluene sulfonate [Sotero et al. (1996)], chlorobenzoate [Carver et al. (1996)], and naphthalenesulfonate [Brown et al. (1989)] have been studied in combination with cationic surfactants because these mixtures can reduce the charge density of surfactant micellar aggregates significantly, enhancing ion pairing and surface activity of the micelles above a minimum hydrotropic concentration (MHC), promoting growth of wormlike micelles at a much lower salt/surfactant ratio in comparison to other salts [Hatzopoulos et al. (2011); Hodgdon and Kaler (2007); Lin et al. (2012); Subramanian et al. (2013)]. In addition, Schubert et al. (2003) reported that adding the hydrotropic salt NaTosylate (0.25 wt. %) could screen the electrostatic interactions and reduce the micellar surface charge in a mixed cationic/anionic wormlike micellar solution consisting of cetyl trimethylammonium tosylate (CTAT, 0.5–4.0 wt. %) and sodium docetyl benzyl sulfonate (SDBS), with [CTAT/SDBS] = 97/3.

In particular, the hydrotropic organic salt SHNC has drawn considerable attention as HNC$^-$ ions have exhibited sensitive responses with varying temperatures, ionic strength, and flow conditions. In addition, mixtures of cationic surfactant and excess amount of SHNC have shown pronounced birefringence phenomena lasting from milliseconds up to even hours after the flow stoppage [Frounfelker et al. (2008); Mishra et al. (1993a)]. Recent studies have used light scattering, flow birefringence, electron microscopy, and rheometric techniques to investigate the material properties of SHNC and cationic surfactant mixtures. Mishra et al. (1993a, 1993b) reported the phase behavior of the mixture of cationic surfactant cetyltrimethylammonium bromide (CTAB) and SHNC. By fixing the CTAB concentration at 60 mM and gradually increasing the CTAB/SHNC molar ratio, the CTAB/SHNC mixture underwent phase transitions from small micellar aggregates to a positively charged gel phase, followed by a liquid crystalline lamellar phase, then precipitated into a multilamellar vesicle phase at equimolar surfactant/salt concentration. In particular, when the concentration ratio of SHNC over cationic surfactant exceeds 1.0, SHNC was observed to inhibit growth or entanglement of micelles by negatively charging micelle surfaces [Abdel-Rahem (2005); Krishnaswamy et al. (2005); Mishra et al. (1993a, 1993b)]. When the temperature increases or the solution is further diluted, the HNC$^-$ ions can actually desorb from the micelles and decrease the surface charge of micelles, which in turn promotes growth of wormlike micelles and enhances the
viscoelasticity of the solution. Notably, the rich phase behavior of CTAB/SHNC mixture is similar to that of the mixture of cationic-anionic surfactant system [CTAB/Sodium dodecyl sulfate (SDS)] as described by Kaler et al. (1989). SHNC is thus considered as an anionic surfactant similar to SDS but with a shorter hydrophobic tail (around 4 nm) [Abdel-Rahem et al. (2005); Hassan et al. (1996); Horbaschek et al. (1998)].

Interestingly, the phase behavior of CTAB/SHNC and CTAB/NaSal shows distinct differences even though SHNC and NaSal are both hydrotropic organic salts that possess the same chemical elements. With fixed CTAB concentration, addition of NaSal also promotes the aggregation of CTAB micelles by screening the electrostatic interaction between surfactant molecules, thereby yielding long and flexible threadlike micelles [Rehage and Hoffmann (1988a); Shikata et al. (1987)]. When the concentration ratio of CTAB/NaSal reaches 1.0, the most stable and rigid micelles are formed in the solution and the linear viscoelasticity of the resulting fluid can be described by a single mode Maxwell model. As the concentration of NaSal increases further, a branched micellar network is observed, with no precipitation or vesicle formations [Rehage and Hoffmann (1988a); Shikata et al. (1987)].

Figure 1 illustrates a side-by-side comparison of the chemical structure of two hydrotropic salts: NaSal and SHNC, and their respective interactions with the cationic surfactant CTAB. NaSal has one benzene ring while SHNC has two fused benzene rings (termed as the naphthalene ring). The numbers shown around the naphthalene ring in Fig. 1(b) represent positions around the naphthalene ring where carboxyl and hydroxyl can be substituted. The green threadlike entities represent wormlike micelles in the solution. In CTAB/SHNC micelles, extra intramolecular forces are introduced by π–π and cation–π interactions.

**FIG. 1.** Chemical structures and schematic representation of the orientation of (a) NaSal and CTAB/NaSal micelles [Manohar et al. (1986)]; (b) SHNC and CTAB/SHNC micelles [Mishra et al. (1993a)]. The numbers represent positions around naphthalene ring where carboxyl and hydroxyl can be substituted. The green dots represent hydrophilic headgroups of CTAB while purple lines represent its hydrophobic tails. The green tube-like entities represent wormlike micelles in solution. In CTAB/SHNC micelles, extra intramolecular forces are introduced by π–π and cation–π interactions.
changes significantly when SHNC is mixed with CTAB solution, in comparison to that of CTAB/NaSal mixtures. As a result, CTAB/SHNC mixtures have shown complex rheological behavior that is associated with higher surface activity and extra intramolecular interactions of micelles [Kalur et al. (2005); Verma et al. (2011)].

The position of the carboxyl and hydroxyl groups in the naphthalene ring of the salt molecule can also play an important role in the wormlike micellar system due to different hydrophobicity. Comparing with SHNC (3,2 HNC), 6-hydroxy-naphthalene-2-carboxylate (6,2 HNC) shares the same chemical compounds as those of SHNC but the carboxyl and hydroxyl groups in the naphthalene ring reside in positions 2 and 6, respectively [see Fig. 1(b)]. For 6,2 HNC and CTAB at equal molar concentrations, multilamellar precipitates were not observed [Abdel-Rahem (2008)]. Brown et al. (1989) studied the mixture of CTAB and sodium naphthalene sulfonate, in which one of the positions in the naphthalene rings was substituted by a single sulfonate ion. The aqueous solution exhibited similar phase behavior and viscoelasticity as those in the mixture of CTAB/NaSal, which remains aqueous in a wide range of salt concentrations [Brown et al. (1989); Hartmann and Cressely (1997); Shikata et al. (1987)]. It was proposed that the combination of the naphthalene structure and the strong hydrophobicity of HNC− was responsible for the unique phase behavior in SHNC-cationic surfactant mixtures [Abdel-Rahem (2008); Rao et al. (1987)].

Most of the existing literature has investigated SHNC/surfactant systems with molar ratios \( R = (\text{salt/surfactant}) \) being 1/1 or greater in cationic surfactant systems. Since semidilute micellar solutions usually possess weak viscoelasticity, they are more desirable for oil recovery and encapsulation related applications with higher mobility. Moreover, cationic surfactant solutions with organic salts in the semidilute regime have shown not only interesting rheological behaviors [Ouchi et al. (2007); Shikata et al. (1987); Vasudevan et al. (2008)] but also exhibited unique capabilities in forming irreversible nanostructured phases [Cardiel et al. (2013); Cardiel et al. (2014b); Dubash et al. (2011); Vasudevan et al. (2010)] for encapsulation and sensing applications [Cardiel et al. (2014a); Lu et al. (2010)]. Motivated by the temperature sensitive nature of SHNC and the advantage of semidilute wormlike micellar solutions, this work focuses on the rheological behavior of aqueous CTAB/SHNC mixtures in the semidilute regime, in which micelles are positively charged and isotropically distributed. Moreover, since we have existing rheological data of CTAB/NaSal system at \( R = (\text{NaSal}/\text{CTAB}) = 0.32 \) [Dubash et al. (2011)], studying CTAB/SHNC systems at \( R = 0.32 \) allows us to understand the influence of the double benzene ring (SHNC) versus the single benzene ring (NaSal) on the rheological properties of CTAB/salt systems. We perform detailed linear and nonlinear rheological characterizations of CTAB/SHNC solution with [CTAB] = 75 mM \( (R = 0.32) \), at different temperatures.

II. MATERIALS AND METHODS

A. Materials

Cationic surfactant CTAB and organic hydrotropic salt NaSal were purchased from Sigma-Aldrich (Saint Louis, MO) and organic hydrotropic salt 3-hydroxy naphthalene-2-carboxylate (SHNC) was purchased from TCI America (Portland, OR), all used as received. The solutions were prepared by adding the appropriate amount of CTAB and SHNC (or NaSal) to deionized water and mixing vigorously for a minimum of 24 h, and left to equilibrate for 1 week. Four different solutions were examined in this work: CTAB concentrations at 40, 60, and 75 mM with fixed molar ratio of \( R = 0.32 \). An aqueous solution containing [CTAB] = 75 mM and NaSal with the molar ratio \( R = 0.32 \) was also studied as a comparison.
B. Rheological measurement principles and methods

1. Linear viscoelasticity of wormlike micelles

Micelles can break and reform continuously. When the kinetic process of micellar breaking and reforming dominates over the timescale for reptation, the micellar solution shows Maxwellian behavior with a single-dominant relaxation time (Cates and Candau (1990); Hoffmann et al. (1985)). The elastic modulus \( G' \) and loss modulus \( G'' \) of the wormlike micellar solution can be described by the Maxwell model with a single stress relaxation time \( \tau_r \),

\[
G'(\omega) = \frac{G_0(\omega \tau_r)^2}{1 + (\omega \tau_r)^2}, \quad G''(\omega) = \frac{G_0\omega \tau_r}{1 + (\omega \tau_r)^2},
\]

where \( \omega \) is the angular frequency and the stress relaxation time \( \tau_r \) can be obtained either as the reciprocal of the \( \omega \) at the crossover of \( G' \) and \( G'' \), or from the above single mode Maxwell model. The plateau modulus \( G_0 \) is extracted by fitting the experimental measurements with the single mode Maxwell and can be related to the micellar mesh size as [Doi and Edwards (1986)]

\[
\xi_m \approx \sqrt{\frac{k_B T}{G_0}},
\]

where \( k_B T \) corresponds to the thermal energy.

On the other hand, when the micelle breakup time is long compared with its reptation time, dynamic properties of the entangled micelles are dominated by reptation [Cates and Candau (1990)]. In the reptation process, stress relaxation is induced by the gradual disentanglements of micellar chains along the curvilinear tube environment, leading to deviations from the single mode Maxwellian behavior and resulting in a spectrum of relaxation times. Shikata and Kotaka (1991) reported that if the micelles were too long and unstable to reptate (i.e., for an equal molar concentration of CTAB and NaSal solution), wormlike micelles could form networks with finite extensibility and sticky temporal crosslinks at entanglement points. These temporal crosslinks can contact and clash with each other with salts serving as catalysts. Granek and Cates (1992) further proposed a Poisson renewal model to study wormlike micellar systems with short breakup times, while the relaxation process is dominated by breathing and local Rouse motion rather than reptation. The effects from breathing and Rouse motion were characterized by an upturn of both \( G'(\omega) \) and \( G''(\omega) \) at higher frequencies in the oscillatory shear flow, exhibiting a dip in the value of \( G''_{\min} \) in the Cole-Cole plot, in which the viscous modulus \( G''(\omega) \) is normalized by the plateau modulus \( G_0 \) and plotted against the normalized elastic modulus \( G'(\omega) \). The depth of the dip in \( G''_{\min} \) found in the Cole-Cole plot can be used to estimate the entangled chain length in wormlike micellar solutions, where the entanglement length is much longer than the persistence length of the micelle. The ratio of the local dip value of \( G'' \) (i.e., \( G''_{\min} \)) with respect to the plateau modulus \( G_0 \) can be used to estimate the average length of the entangled micelles as [Doi and Edwards (1986); Granek and Cates (1992)]

\[
\frac{l_e}{T} \approx \frac{G''_{\min}}{G_0},
\]
where \( l \) represents average micelle length in the micellar system and \( l_e \) is the length of micellar chains between the entanglement points that can be estimated by [Doi and Edwards (1986); Granek and Cates (1992)]

\[
l_e \simeq \frac{\bar{\eta}_m^{5/3}}{l_p^{2/3}},
\]

(4)

where \( l_p \) presents the persistence length of micelles. The persistence length \( l_p \) can be obtained from small-angle neutron scattering measurements. Since \( \bar{\eta}_m \) can be obtained from Eq. (2), the length of micellar chains between the entanglement points \( l_e \) can be estimated by Eq. (4), and the average micelle length \( l \) can then be approximated from Eq. (3). For a wormlike micellar system when \( \tau_b \sim \tau_{rep} \), Eq. (3) is not applicable but provides an upper bound of \( l_e/l \). Hence, the calculated \( l \) can be used as a lower bound for the estimation of the averaged micellar length.

2. Large amplitude oscillatory shear

In the linear viscoelastic regime, the material response is related to the intrinsic properties of the material and is independent of the strain and frequency input. In the nonlinear regime, where the linear viscoelastic model is no longer valid, the evolution of the micellar microstructures under large deformations plays an important role in determining the transient rheological response. Although linear viscoelasticity is useful for understanding the relationship between the microstructure and rheological properties of complex fluids, the linear viscoelastic moduli (\( G' \) and \( G'' \)) are limited by the first harmonic Fourier coefficients of \( G' \) and \( G'' \), which are insufficient to describe the nonlinear material response with a distorted sinusoidal stress response. The LAOS procedure has been employed to provide more detailed information on the viscoelastic response of materials under nonlinear regimes, by capturing higher harmonic Fourier coefficients or Chebyshev coefficients [Ewoldt (2013); Ewoldt et al. (2008)] of stress responses, or fitting experimental data with different viscoelastic models [Blackwell and Ewoldt (2014); Giacomini et al. (2011); Giacomini and Dealy (1998); Gurnon and Wagner (2012); Hyun et al. (2002); Rogers and Lettinga (2012)], by applying different flow procedures [Ewoldt (2013); Rogers (2012); Rogers et al. (2011)].

In fact, materials containing microstructures can exhibit different stress waveforms in the nonlinear regime [Debbaut and Burhin (2002); Dodge and Krieger (1971); Wilhelm (2002)]. For example, Hyun et al. (2006) compared the rheological response of a linear structured polymer solution with a branched polymer solution under LOAS, and observed two different distorted sinusoidal stress waveforms. A Pipkin diagram was built to illustrate the microstructure evolution of complex fluids (such as biopolymer gels, polymer networks, chewing gums, and wormlike micellar solutions) under different strains and frequencies in the nonlinear regime [Ewoldt (2013); Ewoldt et al. (2008); Martinetti et al. (2014)]. The interpretation of nonlinear stress response was based on Chebyshev orthogonal functions correlated with the distinctive response from viscoelastic materials. Comprehensive reviews of interpreting rheological behavior under LOAS flow can be found by Ewoldt (2013); Ewoldt and Bharadwaj (2013); Hyun et al. (2011); and Wilhelm (2002).

In oscillatory shear flows, the material deformation can be described by

\[
\gamma = \gamma_0 \sin(\omega t),
\]

(5)

where \( \omega \) is the angular frequency, \( t \) is the time, and \( \gamma_0 \) is the input strain amplitude. In the linear viscoelastic regime, the stress response is sinusoidal and corresponds to an
elliptical stress curve with respect to the strain. When the strain reaches the nonlinear regime, the stress curve starts to become asymmetric and deviate from the sinusoidal shape. Accordingly, the stress \( (\sigma) \) versus strain \( (\gamma) \) curve (also known as Lissajous-Bowditch curve) would be distorted from the elliptical shape due to the stress contributions at higher harmonics. The normalized higher harmonics represent the degree of distorted stress signals and quantify the nonlinear response. To quantify the degree of the stress distortion, a half-sided (only odd parts for the sine function) discrete Fourier transform can be applied to the stress signal as

\[
\sigma(t) = \sum_{n=1, \text{odd}} \sigma_n \sin(n\omega t + \phi_n),
\]

where \( \sigma_n \) and the phase angle \( \phi_n \) depend on the imposed \( \gamma_0 \) and \( \omega \) [Giacomin and Dealy (1993)]. Neidhöfer et al. (2003) substituted time \( t = t' - \phi/\omega \) to obtain the following relation:

\[
\sigma(t) \propto \sin(\omega t') + I_3 \sin(3\omega t' + \phi_3') + I_5 \sin(5\omega t' + \phi_5') + I_7 \sin(7\omega t' + \phi_7'),
\]

where \( \phi_n' = \phi_n - n\phi_1 \) is the relative phase angle relating to the shape of the stress signal. The odd coefficients \( I_3, I_5, I_7 \) correspond to 3rd, 5th, 7th harmonic coefficients normalized by the first harmonic, respectively, that can be calculated to analyze the nonlinearity of the shear stress under large deformations. Assuming higher harmonic coefficients (i.e., \( I_5, I_7 \)) are negligible, \( \phi_3' \) is the relative phase angle that determines the shape of stress versus time curve, with \( \phi_3' = 0^\circ \) corresponding to a normalized stress curve as a function of time [Daniel et al. (2001)]. At \( \phi_3' = 90^\circ \), the stress versus time curve has backward tilted tendency, while the curve returns to the sinusoidal shape at \( \phi_3' = 180^\circ \), eventually evolving to a “forward tilted shoulder” at \( \phi_3' = 270^\circ \) [Hyun et al. (2002)]. Similar patterns were observed in our experiments. The even harmonics of Fourier series (0th, 2nd, and 4th) have been suggested to be associated with the nonlinearity of normal stress coefficients [Ewoldt (2013); Giacomin and Bird (2011)]. Giacomin and Bird (2011) derived analytical expressions for 0th, 2nd, and 4th harmonics of the second normal stress difference in LAOS by using a nonlinear corotational model and matched their results with the corotational Maxwell model. Ewoldt (2013) pointed out that even harmonics of Fourier series (related to the first normal stress difference) in LAOS highly depended on the input strain representation (whether sine or cosine function). Therefore, we neglect the even harmonics and focus on the odd harmonics in the stress response for the quantification of the LAOS responses in this work.

3. Measurements

The viscoelastic properties of the wormlike micellar solutions were characterized by using a stress controlled rheometer (Anton Paar MCR 502). All measurements were performed by using a stainless steel cone and plate geometry (50 mm diameter and 2° angle) with a truncation gap of 59 \( \mu \text{m} \). Experiments were performed at temperature between 20 and 40 °C. The Anton Paar MCR 502 employs a Peltier element within the base plate and the temperature is maintained stable within ±0.1 °C. We wait 10 min after loading the sample in order for temperature to reach equilibrium before measurements. Considering potential artifacts in the large amplitude characterizations, all measurements were repeated three times and verified by a roughened plate-plate geometry (25 mm in diameter) with a gap size of 500 \( \mu \text{m} \). A solvent trap was used to prevent drying effects.
C. Dynamic light scattering

Dynamic light scattering (DLS) provides a convenient method to probe the dynamic properties of wormlike micellar solutions in a large range of concentrations [Buhler et al. (2004); Cates and Candau (1990); Garg et al. (2006), Nemoto and Kuwahara (1993); Nemoto and Kuwahara (1994); Nemoto et al. (1995); Stepanek et al. (1987); Yin et al. (2009)]. In the semidilute regime of a wormlike micellar solution where a viscoelastic network is formed by entangled and overlapped wormlike micelles, the diffusion coefficient $D$ characterizing the local cooperative diffusion motion in the network [Garg et al. (2006)] can be determined from the measurement of autocorrelation functions of the scattered light $g^{(2)}(\tau, q)$ as

$$g^{(2)}(\tau, q) = A(1 + b|g^{(1)}(\tau, q)|^2),$$

where $A$ is the experimental baseline, $b$ is the spatial coherence factor that depends on the number of coherence areas generating the signal ($0 < b < 1$), $q$ is the scattering vector that can be expressed as $q = (4\pi n/\lambda) \sin(\theta/2)$, with $\lambda$ being the incident laser wavelength, $n$ and $\theta$ being the refractive index of the scattering medium and the scattering angle, respectively. In the dilute regime, $g^{(1)}(\tau, q)$ is a single exponential function with a characteristic time inversely proportional to $q^2$, which characterizes a diffusive behavior. In a polydispersed system with several relaxation times, $g^{(1)}(\tau, q)$ can be analyzed by a constrained regularized CONTIN method [Koppel (1972); Provencher (1976a)] to yield information on the normalized distribution of the decay constant $G(\Gamma)$ as

$$g^{(1)}(\tau, q) = \int_0^\infty G(\Gamma) \exp(-\Gamma\tau) d\Gamma.$$  

This method can be applied to determine the average relaxation time $\tau$ of $g^{(1)}(\tau, q)$ by

$$\tau = \frac{\int G(\Gamma, q) \Gamma d\Gamma}{\int G(\Gamma, q) d\Gamma},$$

Thus, the diffusion constant $D$ can be calculated from [Cates and Candau (1990)]

$$D = \frac{1}{q^2\tau},$$

which can be further related to the hydrodynamic correlation length $\xi_H$, which estimates the mesh size of the micellar network [Cates and Candau (1990); Nemoto and Kuwahara (1993, 1994); Nemoto et al. (1995)]

$$\xi_H = \frac{k_B T}{6\pi \eta_s D} = \frac{k_B T q^2}{6\pi \eta_s \tau},$$

where $k_B T$ is the thermal energy and $\eta_s$ is the solvent viscosity at absolute temperature $T$.

In our work, the hydrodynamic correlation length $\xi_H$ was measured by a DLS apparatus, equipped with a He-Ne laser (Zetasizer Nano ZS, Malvern). The time correlation function measured by DLS was analyzed by a Laplace inversion program (CONTIN) [Koppel (1972); Provencher (1976a, 1976b)]. Experiments were carried out with
temperature ranging from 20 to 40 °C, at a scattering angle of 173° and the wavelength at 633 nm under vacuum setting. Each sample was equilibrated for 20 min before measurements for a given temperature. The correlation length $\xi_H$ of the micellar solution was obtained to evaluate the diffusivity coefficient $D$ of each sample.

We also obtained the polydispersity of the solution from the DLS measurements (Zetasizer Nano ZS, Malvern). In particular, the polydispersity index was calculated from the Cumulants analysis of the DLS-measured intensity autocorrelation function [Koppel (1972); Provencher (1976a, 1976b)]. In the Cumulants analysis, a single particle size mode is assumed and a single exponential fit is applied to the autocorrelation function and the polydispersity describes the width of the assumed Gaussian distribution.

III. RESULTS AND DISCUSSION

To understand the influence of strong bindings of naphthalene rings present in the CTAB/SHNC micellar system, we first examined the linear viscoelasticity of CTAB/SHNC solutions at 25 °C by varying the CTAB concentration while keeping the salt to surfactant concentration ratio fixed at $R = 0.32$, coupled by the DLS measurements. Next, we focused on the semidilute CTAB/SHNC solution at $[\text{CTAB}] = 75$ mM with salt to surfactant (CTAB/SHNC) concentration ratio at $R = 0.32$, and performed linear, transient, and nonlinear rheological characterizations at varying temperatures. Finally, we compared both linear and nonlinear rheology behavior of CTAB/SHNC solution with that of CTAB/NaSal at the same salt and surfactant concentration ($[\text{CTAB}] = 75$ mM), to shed more insight on the double benzene ring effect.

A. Linear and nonlinear rheology at 25 °C with varying CTAB concentrations

The rheological characterizations for micellar solutions at $[\text{CTAB}] = 40, 60,$ and $75$ mM with $[\text{SHNC}]/[\text{CTAB}]$ molar ratio $R = 0.32$ were performed by using a stress controlled rheometer (Anton Paar MCR 502) with a cone and plate geometry, under steady shear and small amplitude oscillatory shear procedures at 25 °C, see Fig. 2. The rheological parameters are summarized in Table I. For 60 and 75 mM CTAB/SHNC solutions, the plateau modulus $G_0$ and relaxation time $\tau_r$ (cross over of $G'$ and $G''$) were determined directly from the frequency sweep data. For 40 mM CTAB/SHNC solution, $G_0$ and $\tau_r$ were obtained by fitting the experimental data to a single mode Maxwell model (see detailed fit information in the supplementary material).

In Fig. 2(a), a dramatic increase in zero shear viscosity $\eta_0$ at $[\text{CTAB}] = 60$ (~100 Pa s) and $75$ mM (~1000 Pa s) was observed when compared with that of 40 mM CTAB/SHNC solution, indicating a substantial length increase of wormlike micelles at higher surfactant concentrations [Khatory et al. (1993)]. In particular, CTAB/SHNC solutions at $[\text{CTAB}] = 60$ mM and $75$ mM exhibited strong shear thinning behavior in more than three decades of shear rates and $\eta(\dot{\gamma})$ was well fitted by a power law relation with the power index $n = -0.88 \pm 0.21$. In the shear stress versus shear rate curves [Fig. 2(b)], stress plateau was observed for 40 mM CTAB/SHNC solution at a narrow shear rate range, while 60 mM CTAB/SHNC solution exhibited typical shear banding behavior with a shear stress plateau $\sigma_p$ extending between low and high shear rates branches in the wormlike micellar solution [Berret (1997); Berret et al. (1994); Britton et al. (1999); Fielding and Wilson (2010); Lerouge and Berret (2010); Lerouge et al. (1998); Lerouge et al. (2008); Moorcroft and Fielding (2014)]. In contrast to the 60 mM solution, $75$ mM CTAB/SHNC solution achieved a $\sigma_{\text{max}}$ much larger than the stress plateau $\sigma_p$ at a low shear rate $\dot{\gamma}_1$ before
reaching the shear stress plateau. Grand et al. (1997) suggested that the appearance of a stress maximum was indicative of the existence of a transient branch with a stress larger than \( r_p \). It was proposed that the maximum shear stress could be estimated by \( r_{\text{max}} = 0.67G_0 \) (\( G_0 \) the plateau modulus), occurring at a shear rate of \( \dot{\gamma}_1 = 2.6/\tau_r \) for an ideal Maxwell fluid [Berret et al. (1994); Cates (1990); Grand et al. (1997)]. Since our 75 mM CTAB/SHNC solution is not an ideal Maxwell fluid, we observed that \( r_{\text{max}}/C_24^0.64G_0 \) and the critical shear rate for the maximum stress was around \( \dot{\gamma}_1 = 1.1/\tau_r \) (\( \tau_r = 100.4 \) s) [see Fig. 2(b)]. Nevertheless the product of \( \dot{\gamma}_1 \times \tau_r = 1.1 \) lies within the range of (0.94–1.53), consistent with the range of values reported for wormlike micellar systems with nonideal Maxwellian behavior [Grand et al. (1997)]. Figure 2(c) shows the elastic modulus \( G_0 \) and

![Graphs showing shear viscosity, shear stress, elastic modulus, and Cole-Cole plots for three CTAB/SHNC solutions at 25 °C.](image)

**FIG. 2.** All three CTAB/SHNC solutions at 25 °C: (a) Shear viscosity and (b) shear stress as a function of shear rate under steady shear procedure; (c) the elastic modulus (\( G' \), filled symbols) and viscous modulus (\( G'' \), open symbols) are plotted as a function of frequency under small amplitude oscillatory shear at 10% strain in a cone and plate geometry; (d) normalized Cole-Cole plots.

| Samples | \( \eta_0 \) (Pa s) | \( G_0 \) (Pa) | \( \tau_r \) (s) | \( \zeta_m \) (nm) | \( \zeta_H \) (nm) | \( D \) (10^{-10} m²/s) | Polydispersity |
|---------|------------------|--------------|---------------|----------------|----------------|-------------------|----------------|
| 40 mM*  | 0.20 ± 0.02      | 1.2 ± 0.5   | 0.3 ± 0.1     | 202 ± 12       | 14.5 ± 1.9     | 0.15 ± 0.03       | 0.33 ± 0.06     |
| 60 mM*  | 100 ± 5          | 10 ± 1      | 50.3 ± 0.5    | 74.4 ± 7.5     | 12.5 ± 1.5     | 0.17 ± 0.03       | 0.32 ± 0.05     |
| 75 mM*  | 1000 ± 9         | 13 ± 2      | 101 ± 2       | 68.1 ± 7.6     | 11.3 ± 1.2     | 0.19 ± 0.04       | 0.28 ± 0.04     |
| 75 mM*  | 2.5 ± 0.3        | 6.0 ± 0.6   | 0.21 ± 0.03   | 88.2 ± 8.9     | 10.0 ± 1.3     | 0.21 ± 0.04       | 0.29 ± 0.04     |
| 100 mM* | 126 ± 2          | 12 ± 2      | 6.4 ± 0.7     | 60.3 ± 5.9     | 7.8 ± 0.9      | 0.27 ± 0.05       | 0.26 ± 0.02     |

*From Dubash et al. (2012) with CTAB/NaSal system, *CTAB/SHNC system.
viscous modulus $G''$ being plotted against the frequency $\omega$ in the linear viscoelastic regime at 10% strain for all three solutions, at 25 °C. The stress relaxation time $\tau_r$ for 60 and 75 mM CTAB/SHNC solutions can be obtained from the crossover frequencies while 40 mM CTAB/SHNC solution showed weakly viscoelastic response without a crossover in the frequency range tested. Normalized Cole-Cole plots for all three solutions are shown in Fig. 2(d) with the solid black curve corresponding to the single-mode Maxwellian linear viscoelastic model. Figure 2(d) illustrates that viscoelastic 75 mM CTAB/SHNC solution does not follow the single-mode Maxwellian model, while 40 and 60 mM CTAB/SHNC solutions deviate even further from the semicircle and no obvious $G''$ is observed. Shikata et al. (1988a) argued that the deviation from the single Maxwell model behavior was caused by the low salt to surfactant molar ratio and low surfactant concentrations, with wormlike micelles in varying lengths in solutions (see Table I), leading to a spectrum of relaxation times.

Compared with the linear rheological characterizations at 25 °C performed by Dubash et al. (2012) with the same surfactant $[\text{CTAB}] = 75$ and $100$ mM (NaSal)/[CTAB] = 0.32), a similar trend of increasing viscoelasticity with increasing CTAB concentration was observed, see Table I. We observed that zero shear viscosity $\eta_0$ and relaxation time $\tau_r$ were 3 orders of magnitude higher in the 75 mM CTAB/SHNC solution than those of 75 mM CTAB/NaSal solution, while the plateau modulus $G_0$ was only two times higher. In the entangled regime, plateau modulus $G_0$ only depends on the entanglement mesh size; thus, the difference in these rheological parameters would be indicative of micelle persistence length difference in CTAB/NaSal and CTAB/SHNC systems. Note that the 75 and 100 mM CTAB/NaSal solutions reached a nonmonotonic shear stress plateau without any stress maximum $[\text{Dubash et al. (2012)}]$, which is consistent with the argument that the counterions from the salt at the micelle surface may change the micelle stiffness and interactions between the neighboring micelles $[\text{Mishra et al. (1993a, 1993b)}]$. On the one hand, the extra tail in CTAB/SHNC reduces the curvature of CTAB micelles more significantly when compared with the CTAB/NaSal micelles, facilitating elongated micelle formation with smaller packing parameters in CTAB/SHNC micelles. On the other hand, the naphthalene structure in CTAB/SHNC micelles is more hydrophobic than the salicylate ions in CTAB/NaSal micelles. In order to shield themselves from water, the HNC$^-$ ions tend to form either $\pi-\pi$ bonds with another naphthalene ring or cation-$\pi$ bonds with adjacent hydrophobic CTAB headgroups, as illustrated in Fig. 1. These noncovalent bonds are much stronger than hydrogen bonds, and can increase the shear viscosity and micelle relaxation time of CTAB/SHNC solutions significantly. This argument can be applied to another set of sample parameters: the $\eta_0$ and $G_0$ in 60 mM CTAB/SHNC solution are comparable with those in 100 mM CTAB/NaSal solution, but the relaxation time $\tau_r$ in 60 mM CTAB/SHNC solution is much longer when compared with that of 100 mM CTAB/NaSal solution, due to stronger interactions between noncovalent bonds and high viscosity in the CTAB/SHNC solution which hinder the breakup of micelles in the system $[\text{Kalur et al. (2005)}]$. The diffusivity constant $D$ and hydrodynamic correlation length $\xi_H$ for all three CTAB/SHNC solutions were obtained by performing DLS (see Sec. II for experimental details), as shown in Table I. Nemoto and Kuwahara (1993, 1994) and Nemoto et al. (1995) reported that the diffusion coefficient $D$ depended on both surfactant concentration $C_d$ and salt to surfactant concentration ratio $R$ in an aqueous CTAB/NaSal solution. When a small amount of salt was added, the wormlike micellar network would entangle while the electrostatic repulsion would increase the diffusivity $D$ and suppress the hydrodynamic correlation length $\xi_H$, see Eq. (12). Cates and Candau (1990) suggested that scaling prediction of hydrodynamic correlation length $\xi_H$ on surfactant concentration could be inferred from the scaling of micelle mesh size $\xi_M$, if the average micelle size was large compared with the network mesh size. However, this argument was not valid
in CTAB/SHNC solutions with low salt concentration, which exhibit polydispersity in micelle length and deviation from the single Maxwell model (see the polydispersity information in Table I). Cates and Candau (1990) also proposed that the monotonic decrease of $\xi_H$ with increasing surfactant concentrations implied strong interactions among micelles, either through the entanglements or through the formation of micelle crosslinks. Since the crosslink formation in CTAB/SHNC system is not favorable with a low decreasing exponent of $\xi_H$ ($\sim 0.1$), the entangled micelle network is likely to be more dominant in our CTAB/SHNC solutions.

Among the three CTAB/SHNC solutions examined, a distinct stress bump was observed for 75 mM CTAB/SHNC solution [see Fig. 2(b)], implying possible transient behavior induced by double benzene rings in the system. To further investigate the binding stability of naphthalene micelles in 75 mM CTAB/SHNC solution, we conducted systematic linear, transient, and nonlinear rheological characterizations with temperatures varying from 20 to 40 °C, with comparisons to that of 75 mM CTAB/NaSal solution, see details below.

B. Rheological characterizations of 75 mM CTAB/SHNC solution

1. Linear rheology at elevated temperatures

Steady shear flow and small amplitude shear oscillations were performed on 75 mM CTAB/SHNC solution at temperatures between 20 and 40 °C. Comparison in steady shear flow behavior was made between CTAB/SHNC and CTAB/NaSal solutions ([CTAB] = 75 mM) at selected temperatures (see Table II). Figure 3(a) shows that CTAB/SHNC solution shear thinned and $\eta(\dot{\gamma})$ can be fitted by a power law index of $n = -0.88 \pm 0.21$ for all temperatures. Even though zero shear viscosity $\eta_0$ dropped dramatically with increasing temperatures, $\eta_0$ remained above 2 Pa·s at 40 °C and exhibited shear thinning at higher shear rates. On the contrary, the single benzene ring system (75 mM CTAB/NaSal solution) was even more sensitive to temperature variations [see inset in Fig. 3(a)], with $\eta_0$ reducing to $\leq 0.01$ Pa·s at 40 °C and behaving like a Newtonian fluid. Table II tabulates all the key rheological parameters from these measurements. The relative stability at high temperatures for the CTAB/SHNC system can be attributed to the long relaxation time of micelles with strong noncovalent interactions from the naphthalene ring. In addition, HNC$^-$ ions become less hydrophobic at higher temperatures, adapting to a closer binding to the micellar surface to prevent micelle breakup. In Fig. 3(b), a maximum shear stress was observed at 20 and 25 °C around shear rates $\dot{\gamma}_1 \sim 1.1/\tau_r \approx 0.01$ s$^{-1}$, followed by a shear stress plateau. At higher temperatures, stress overshoot was significantly diminished before reaching a shear stress plateau.

The shear stress overshoot has been reported by Grand et al. (1997) of aqueous CPyCl/NaSal (100/60 mM) system, in the temperature range of 20–25 °C. The steady state shear rate $\dot{\gamma}$ in the low shear band corresponded to the largest shear stress $\sigma$. This

| T (°C) | $\eta_0$ (Pa·s) | $G_0$ (Pa) | $G''_{\mathrm{max}}$ (Pa) | $\frac{G''_{\mathrm{max}}}{G_0}$ | $\tau_r$ (s) |
|-------|-----------------|------------|------------------------|--------------------------|-------------|
| 20    | 3920 ± 40       | 13 ± 2     | 0.30 ± 0.04            | 0.02 ± 0.03              | 317 ± 3.0   |
| 25    | 10000 ± 9       | 13 ± 2     | 1.1 ± 0.3              | 0.09 ± 0.01              | 101 ± 2.0   |
| 30    | 240 ± 21        | 13 ± 2     | 2.0 ± 0.3              | 0.15 ± 0.02              | 25.2 ± 3.3  |
| 35    | 47 ± 5          | 12 ± 2     | 3.6 ± 0.5              | 0.30 ± 0.04              | 3.2 ± 0.6   |
| 40    | 1.8 ± 0.2       | 11 ± 1     | 5.0 ± 0.5              | 0.45 ± 0.03              | 0.41 ± 0.04 |
stress overshoot was termed as “top-jumping,” in which case a transient branch exists with a stress larger than the shear stress plateau \( \sigma_p \). The time scale to relax this transient state to a “truly” steady state flow is much longer than the Maxwell relaxation time of the micellar solution. Grand et al. (1997) estimated this time scale \( \sim (\dot{\gamma} - \dot{\gamma}_c)^{-p} \), with \( p \) depending on the chemical composition and temperature of the solution. Berret et al. (1994) also observed a stress overshoot in a 0.5 M NaCl solution containing CPyCl and NaSal (\( \mathcal{R} = 0.5 \) with total surfactant concentration of 12%). Their stress overshoot was due to the nucleation and growth of a shear induced nematic phase, which is not applicable to our low weight fraction (\( \phi < 5\% \)) surfactant system. More discussion can be found in Sec. III B 2.

![Graph](image-url)
In Fig. 4(a), we plot the elastic modulus $G'$ and viscous modulus $G''$ versus the angular frequency $\omega$ in the linear viscoelastic regime with $10\%$ strain, for $20$–$40^\circ C$. The stress relaxation time $\tau_r$ was then determined from the first crossover point of $G'$ and $G''$ curves and a descending trend was observed with increasing temperatures. The plateau modulus $G_0$ was obtained as the plateau value of $G'$ from Fig. 4(a), listed in Table III. The key rheological parameters (i.e., $\eta_0$ and $\tau_r$) were very sensitive to temperature variations and could be described by the Arrhenius relations in Cates and Candau (1990)

$$\tau_r = A \exp \left( \frac{E_a}{RT} \right) \quad \text{and} \quad \eta_0 = G_0 A \exp \left( \frac{E_a}{RT} \right),$$

(13)

where $E_a$ is the flow activation energy, $\bar{R}$ is the gas constant, and $T$ is the absolute temperature. The inset in Fig. 4(a) showed that both $\tau_r$ and $\eta_0$ could be linearly scaled with $1000/T$ with similar slopes. The flow activation energy $E_a$ obtained from the $\tau_r$ Arrhenius relationship yielded $E_a \sim 192.3 \text{ kJ/mol}$, while the $\eta_0$ Arrhenius relationship resulted $E_a \sim 206 \text{ kJ/mol}$. These two estimated $E_a$ values are within $7\%$ difference and are also consistent with previous reported range of $E_a$ values (70–300 kJ/mol) by Han et al. (2011). The plateau modulus $G_0$ extracted from the Arrhenius relation ($G_0 \sim 13 \text{ Pa}$)

![Fig. 4](image-url)

**FIG. 4.** (a) The storage modulus ($G'$, filled symbols) and loss modulus ($G''$, open symbols) as a function of frequency for 75 mM CTAB/SHNC solution at different temperatures under small amplitude oscillatory shear flow. The inset exhibited the Arrhenius relations for $\tau_r$ and $\eta_0$ at five varying temperatures. (b) Normalized Cole–Cole plots for 75 mM CTAB/SHNC solution at different temperatures.
is also consistent with the frequency sweep measurements at varying temperatures, indicating that although the average micelle length decreased in the system as a function of temperature, the micelles maintained its flow activation energy.

Normalized Cole-Cole plots for 75 mM CTAB/SHNC at four different temperatures are shown in Fig. 4(b) with the solid black curve corresponding to the single mode Maxwell model. All curves agree well with the semicircle at low frequencies, but display an increasing deviation from the semicircle with increasing frequencies, accompanied by an apparent dip of $G''_{\text{min}}$ and an upturn of $G''$, which are related to Rouse and breathing modes by Granek and Cates (1992). The depth of $G''_{\text{min}}$ in the experimental data provides a semiquantitative estimate of the ratio of $l_c/\bar{l}$ by Eq. (3), where $\bar{l}$ represents average micellar length in the system and $l_c$ is the length for micellar chains between entangled points. At 20 and 25°C, the ratio of $G''_{\text{min}}/G_0$ is 0.02 and 0.09, respectively, suggesting that the average chain length $\bar{l}$ is much longer than the micelle entanglement length, consistent with the fact that $\eta_0$ and relaxation time $\tau_r$ are higher at the 25°C. When the ratio of $G''_{\text{min}}/G_0$ increased further, the dip of $G''_{\text{min}}$ got shallower at 30°C and finally disappeared at 35 and 40°C, in which case the micelle chains were only a few times of the entanglement length and the micelle breakup time became comparable with the entanglement time.

Following the Poisson renewal model, we estimated the entanglement mesh size $\xi_m$ from Eq. (2) and further obtained the entanglement length $l_e$ and the average micelle length $l$ of 75 mM CTAB/SHNC solution from Eqs. (3) to (4), respectively, see Table III. Note that a significant decrease of $\bar{l}$ and $\tau_r$ was observed while the entanglement mesh size $\xi_m$ was not strongly affected by elevating temperatures, implying that entangled micellar network almost remained intact even though the micelles were easier to break and reform at high temperatures. This observation is consistent with the hydrodynamic correlation length obtained from the DLS measurements. A monotonic increase in micelle diffusivity $D$ implies increasing thermal agitation of micelles, while the corresponding $\xi_H$ remained $\sim 10 \pm 1.5$ nm for all temperatures tested, suggesting that the hydrodynamic properties in the CTAB/SHNC solution were not strongly affected in the temperature range we investigated [Nemoto et al. (1995)]. However, the competition between various time scales under elevating temperatures can yield interesting transient and nonlinear rheological behaviors, see details below.

### 2. Transient rheology

Hydrophobic HNC$^-$ ions have shown sensitive temperature responses: HNC$^-$ ions can desorb from the micellar surface, where $\pi-\pi$ and cation–$\pi$ bonds between micelles become weakened with increasing temperatures with excessive HNC$^-$ in a micellar solution [Kalur et al. (2005)]. Here, we employed both startup shear and shear hysteresis flow procedures to probe the transient rheology behavior of 75 mM CTAB/SHNC solution.

#### TABLE III. Characteristic length of 75 mM CTAB/SHNC solution at different temperatures.

| T (°C) | $\xi_m$ (nm) | $l_e$ (nm) | $\bar{l}$ (μm) | $\xi_H$ (nm) | $D \times 10^{-10}$ (m$^2$/s) |
|-------|--------------|------------|----------------|--------------|-------------------------------|
| 20    | $67.8 \pm 7.5$ | $185 \pm 15$ | $9.3 \pm 1.5$ | $12.6 \pm 1.3$ | $0.16 \pm 0.03$               |
| 25    | $68.1 \pm 7.6$ | $187 \pm 15$ | $2.1 \pm 0.2$ | $11.3 \pm 1.2$ | $0.19 \pm 0.04$               |
| 30    | $68.5 \pm 7.9$ | $189 \pm 17$ | $0.95 \pm 0.13$ | $9.8 \pm 1.1$ | $0.23 \pm 0.05$               |
| 35    | $70.8 \pm 8.2$ | $199 \pm 19$ | $0.62 \pm 0.06$ | $8.7 \pm 0.9$ | $0.26 \pm 0.05$               |
| 40    | $73.2 \pm 8.9$ | $211 \pm 20$ | $0.41 \pm 0.03$ | $8.2 \pm 0.9$  | $0.30 \pm 0.06$               |
a. Startup shear. Since a pronounced stress overshoot of 75 mM CTAB/SHNC solution was observed at 20°C [orange curve in Fig. 3(b)], shear stress $\sigma$ was plotted against shear strain $\gamma$ at different shear rates ($\dot{\gamma} = 0.001 - 10$ s$^{-1}$) at 20°C, see Fig. 5. In the upper inset, we plotted shear stress versus shear rate from the steady shear flow procedure and divided into 2 regimes. Regime 1 is the low shear rate branch/elastic deformation regime where shear rate $10^{-3} \leq \dot{\gamma} \leq 0.005$ s$^{-1}$. Regime 2 is the shear banding regime where $0.01 \leq \dot{\gamma} \leq 10$ s$^{-1}$. In the shear banding regime, homogeneous flow of wormlike micellar solutions can become unstable and separate into coexisting shear bands with different local viscosities and internal structures [Cappelaere et al. (1995, 1997); Rehage and Hoffmann (1991)]. Macroscopic rheology coupled with local measurements such as nuclear magnetic resonance [Britton and Callaghan (1997); Holmes et al. (2004)], DLS [Salmon et al. (2003)], PIV (particle tracking velocimetry) [Hu and Lips (2005)], high frequency ultrasonic velocimetry [Becu et al. (2004); Manneville et al. (2004)], rheo-optics [Lerouge and Berret (2010)], spatially resolved SANS measurements in the flow-gradient plane [Helgeson et al. (2009a, 2009b); Liberatore et al. (2006, 2009)], and a combination of different techniques have been widely used to explore the complex spatio-temporal dynamics in the heterogeneous structures at the shear plateau regime [Berret et al. (1997, 1994); Berret (1997); Bhattacharjee et al. (2003); Decruppe et al. (2006); Fardin et al. (2010, 2011, 2012); Fielding (2007); Fielding and Wilson (2010); Fischer et al. (2002); Lee et al. (2005); Lerouge et al. (1998); Miller and Rothstein (2007)].

Lower shear rates ($\dot{\gamma} = 0.001$ and 0.005 s$^{-1}$) were chosen in the low shear rate regime prior to shear banding. The maximum shear stress $\sigma$ increased monotonically with imposed strain $\gamma$ and continuous shear deformation. When the shear rate exceeds the reciprocal of the relaxation time $1/\tau_r$ ($\dot{\gamma} \sim 0.01$ s$^{-1}$), $\sigma$ reaches a maximum, then decreases over time. Shear rate $\dot{\gamma} = 0.01$ s$^{-1}$ corresponds to the onset of the shear banding plateau. Within this shear rate range, the stress versus strain curves for all chosen shear rates exhibit a similar slope before reaching the maximum shear stress, and the shear stress would eventually approach a value that is consistent with the shear stress plateau $\sigma_p$, at
different time scales for different shear rates (see light blue and gold curves). The relatively long time scale (longer than the stress relaxation time) to reach $\sigma_p$ value is potentially related to micelles slowly relaxing back to a shear banding state, or caused by the chain alignment and orientation induced by shear deformation [Lu et al. (2014)].

Since startup experiments are susceptible to wall slippage [Gurnon et al. (2014); Hu et al. (2014); Hu and Lips (2005); Lin et al. (2012)] and flow heterogeneities in shear banding flow [Mewis and Wagner (2009)], nonlinear rheological characterizations were required to shed more insight.

**b. Shear hysteresis.** Shear hysteresis characterizations have been widely studied in gel-like fluids with thixotropic and viscoelastic properties [Bird and Marsh (1968); Divoux et al. (2013); Mewis and Wagner (2009); Yoon et al. (2014)]. The shear rate usually starts from a maximum value before being swept down to $10^{-3}$ 1/s, and ramped up to the original maximum value. Transient shear stress can be plotted as a function of the shear rate and a hysteresis loop can be formed due to the lag between the shear stress and shear rate. The shape and area of the hysteresis loop are dependent on the shear history of a given material [Mewis and Wagner (2009)]. We investigated the shear hysteresis behavior for 75 mM CTAB/SHNC solution at 20, 25, and 35°C, respectively, see Fig. 6.

**FIG. 6.** Flow curves of $\sigma$ vs $\dot{\gamma}$ of 75 mM CTAB/SHNC by ramping down the shear rate from $\dot{\gamma}_{up} = 10$ s$^{-1}$ to $\dot{\gamma}_{down} = 10^{-3}$ s$^{-1}$ (filled symbols) and ramping up from $\dot{\gamma}_{down}$ to $\dot{\gamma}_{up}$ (open symbols) at (a1–a3) 20°C; (b1–b3) 25°C; (c1–c3) 35°C. Different shear ramp durations related to the stress relaxation time at each temperature are marked in each sub-figure.
The initial shear rate was set to be $\dot{\gamma}_{\text{up}} = 10 \text{ s}^{-1}$, then swept down to a low shear rate $\dot{\gamma}_{\text{down}} = 10^{-3} \text{ s}^{-1}$ (filled symbols), and subsequently increased back to $\dot{\gamma}_{\text{up}}$ (open symbols). Various time steps related to micelle relaxation times (approximately the same, half of, or 1/10th of) were chosen at different temperatures, see Fig. 6. The maximum shear rate ($10 \text{ s}^{-1}$) was selected to ensure samples were not expelled from the geometry gap in any of the measurements. The data in Fig. 6 were collected by using a 50 mm and 1$^\circ$ smooth cone-plate geometry. We confirmed that neither slip nor the shearing sequence (down–up and up–down) affected the results by performing similar testing using a 25 mm roughened parallel plate (see supplementary material).

Referring to Table III, the stress relaxation time of 75 mM CTAB/SHNC solution is around 317 s at 20°C. By employing the slowest ramping rate $\delta t \sim \lambda \sim 300 \text{ s}$, shear stress $\sigma$ decreased sharply with decreasing shear rates first [red curve in Fig. 6(a1)], indicating an initial quenching/alignment of micelles under high shear rates. However, a slow recovery of shear stress appeared when $\dot{\gamma}_{\text{down}} < 0.01 \text{ s}^{-1}$, with possible reconstruction of the micellar network since the ramping rate $\delta t$ was very close to the micelle relaxation time. A stress overshoot emerged when the shear rates ramped up again, around $0.005 \text{ s}^{-1}$, which likely originated from heterogeneous shear bands. At faster ramping rates ($\delta t = 150 \text{ s}$ and $\delta t = 30 \text{ s}$), the recovery of shear stress when ramping down was much less significant compared with $\delta t = 300 \text{ s}$ [see Figs. 6(a2) and 6(a3)], since the micelles did not have time to reconstruct the gel network. However, the stress overshoot in the ramp up segment was still observed at higher shear rates with an increasing area of stress hysteresis loop.

At 25°C, the stress relaxation time of 75 mM CTAB/SHNC solution is around 100 s. We again selected three distinct ramping rates corresponding to $1$, $0.5$, and $0.1$ of the stress relaxation time. The stress overshoot and evolution trend at 25°C are similar to those shown at 20°C, but the stress was almost fully recovered when the ramping rate was equal to the micellar relaxation time at $\delta t = 100 \text{ s}$, see Fig. 6(b1). Micelle contour length fluctuations [Milner and McLeish (1998); Milner et al. (2001)], micelle chain stretch and convective constraint release (CCR) mechanism [Bhattacharjee et al. (2003); Graham et al. (2003); Ianniruberto and Marrucci (2002)] have been widely studied to complement Doi-Edwards’s tube model [Doi and Edwards (1986)] and Poisson renewal model [Granek and Cates (1992)] by illustrating the transient stress response for shear thinning fluids. In our case, the micelles were initially stretched at high shear rates, the decrease of shear rates not only led to the stretch relaxation in the entangled network but also enhanced the influence of the constraint release (the relaxation of oriented anisotropic micelles). The intramolecular interactions of noncovalent $\pi-\pi$ and cation–$\pi$ bonds became less favorable at 25°C and entangled micelles can be relaxed and reoriented more easily.

At 35°C, shear hysteresis patterns are different from those at 20 and 25°C. The structures were able to fully recover at the slowest ramping rate $\delta t = 30 \text{ s}$. When the ramping rates increased to 6 s shown in Fig. 6(c2) and 3 s in Fig. 6(c3), the residual stress increased rapidly with $\dot{\gamma}_{\text{up}}$, as the stress accumulated with the deformation before inducing breakage of micellar structures. This type of hysteresis loop has been reported in suspensions, foams, and granular materials [Da Cruz et al. (2002)]. The shear hysteresis loop revealed an apparent transition from strong thixotropic behavior at low temperatures to shear thinning property at higher temperatures in CTAB/SHNC wormlike micellar system.

3. Nonlinear rheology: LAOS flow

Since linear rheology provides limited information related to microstructural transitions in wormlike micellar solutions under flow, we conducted nonlinear rheological
characterizations with large amplitude oscillatory shear (LAOS) flows to further reveal the naphthalene ring influence in the micellar solutions under oscillatory flow field. LAOS employs accurate sinusoidal strain input to probe the microstructural transitions in a sample without causing edge failure of the sample [Blackwell and Ewoldt (2014)]. Accompanied by the results from linear and transient rheology procedures, LAOS illustrates a comprehensive picture of how wormlike micelles are affected by the cyclic switching on and off of the flow. As discussed earlier, the naphthalene ring can easily form stable noncovalent bonds that “arrest” micelles under simple shear flows and small deformations [Frounfelker et al. (2008)]. We envision that noncovalent bonds in CTAB/SHNC wormlike micellar solutions can be potentially decomposed under large deformations and thermal agitations. We focused on 75 mM CTAB/SHNC solution for the LAOS characterization in this section not only because of its strong viscoelastic properties but also because its rheological properties can be compared with those of 75 mM CTAB/NaSal solution.

First, a strain sweep of strain $\gamma = 1\% - 1000\%$ for 75 mM CTAB/SHNC solution from 20 to 35°C was performed in order to identify its linear/nonlinear viscoelastic regimes, shown in Fig. 7. Hyun et al. (2002, 2011) classified four types of LAOS response of complex fluids based on the strain sweep procedure: type I, strain thinning (both $G'$ and $G''$ decreasing with increasing strains); type II, strain hardening (both $G'$ and $G''$ increasing); type III, weak strain overshoot ($G'$ decreasing, $G''$ increasing followed by decreasing); type IV, strong strain overshoot ($G'$ and $G''$ both increasing followed by decreasing). There was a weak overshoot of $G''$ at both 20 and 25°C, corresponding to type III response. At 35°C, the strain overshoot was smoothed out with a decrease in both $G'$ and $G''$, corresponding to type I behavior. This strain sweep measurement provides limited insight of microstructure transition in the nonlinear regime. For example, the overshoot of $G''$ in type III response could be either due to the breakup and reformation of microstructures, or the viscous dissipation among microstructural clusters in the material [Hyun et al. (2002, 2011)]. Thus, even though type III behavior was observed for both 20 and 25°C, further information in the nonlinear viscoelastic regime is needed to capture the microstructure evolution under flow by using LAOS measurements.

For 75 mM CTAB/SHNC solution, LAOS measurements were conducted by applying sinusoidal strain signals at $\gamma$ of 10%, 50%, 100%, 500%, and 800% at a fixed angular frequency $\omega = 0.07$ rad/s, for three different temperatures (20, 25, and 35°C). The Deborah number De is defined as $De = \tau_x \times \omega$, and the Weissenberg number $Wi = \gamma \times De$. Figure 8(a) shows the shear stress (σ) response as a function of time and Lissajous normalized shear stress $\sigma$ versus shear strain $\gamma$ curves [Fig. 8(b)] at 20°C. At $\gamma = 10\%$ and 50%, $\sigma$ versus $\gamma$ plots show a linear trend with a phase angle $\approx 45^\circ$, consistent with the linear viscoelastic response shown in Fig. 7(a). At higher strains $\gamma = 100\%, 500\%,$ and 800%,

**FIG. 7.** Strain sweep for 75 mM CTAB/SHNC at (a) 20°C; (b) 25°C; (c) 35°C from $\gamma = 1\% - 1000\%$ of strain and a frequency of 0.07 rad/s.
the viscoelastic response becomes evident with an increase in the phase angle, reflected by a sinusoidal stress response with time [Fig. 8(a)] and elliptical Lissajous curves [Fig. 8(b)]. To quantify the degree of nonlinearity in the stress response, higher order Fourier harmonic coefficients $I_n$ [using Eqs. (6) and (7)] were calculated by Fourier transforms of stress in the frequency domain and normalized by the first harmonic coefficient $I_1(\omega_1)$, see Fig. 8(c). The magnitude of these normalized coefficients can quantify the nonlinearity of the shear stress under large deformations. With increasing strain $\gamma$, $I_3$ and $I_5$ reached an asymptote with magnitudes less than 0.06 and a vanishing coefficient $I_7$.

At 20°C, the stress relaxation time obtained from the SAOS measurement ($\tau_r \sim 317$ s, see Table III) is greater than the deformation time ($1/\omega \sim 100$ s) from the LAOS oscillation, hence the micelles were continuously deforming without being completely relaxed. It has been proposed that entangled wormlike micellar networks would “yield” when the time scale introduced by the flow is shorter than the intrinsic time scale (relaxation time $\tau_r$) of the system. The “yield like” behavior exhibited in these systems is due to the entangled/disentangled micelle chains [Tapadia and Wang (2004, 2006)], especially under periodic flow at large amplitudes. The imbalance of two forces, the elastic retraction force from shear, and the extension force from the entanglement points can induce disentangled chains, accompanied by the homogeneous elastic deformation within wormlike micellar networks [Wang et al. (2013)]. In our case ($\tau_r > 1/\omega$), with increasing strain $\gamma$, the micellar networks kept on yielding and the stress was more likely to accumulate and relax in the entangled network, accompanied by the viscous dissipation during the deformation period.

At higher temperature 25°C, linear viscoelastic response in 75 mM CTAB/SHNC solution was observed at $\gamma = 10\%$ from the LAOS measurement. However, the micellar solution exhibited high nonlinearities with tilted stress curves (marked in Fig. 9) when $\gamma \geq 50\%$,
showing a nonlinear viscoelastic response with distorted sinusoidal shaped stress versus time curve (forward tilted stress) and deformed elliptical shape of the Lissajous curve. Hyun et al. (2006) observed similar deviations from sinusoidal shaped stress versus time response in a 4 wt. % aqueous Xanthan gum solution. They proposed that the “forward tilted stress” was related to the linear chain structures that were isotropically distributed in the Xanthan gum solution, which may also align and associate to form a structured gel. The sharp increase in the stress signal in the Lissajous curve, termed as the “sticking” stress by Hyun et al. (2006), was caused by short range potentials between two charged headgroups of polymer chains. At $\gamma = 500\%$ and 800%, we also observed stress bumps in the stress versus time curves, see Fig. 9. Rogers et al. (2011) also reported a stress bump for a soft colloidal solution under LAOS. They proposed the concept of the “cage” strain causing the stress bump: the colloidal glass system displayed an elastic response and sustained the deformation before reaching the cage strain. The stress buildup and breaking of microstructures consequently led to the stress bump. This “stick-slip” system would flow again when the strain rate reached zero, until the cage reformed and another stick-slip cycle began.

For our CTAB/SHNC solution at 25°C, the structured micellar network was first deconstructed due to large deformation $\gamma$. However, since the deformation time scale $1/\omega \sim 100$ s is very close to the longest micelle relaxation time, new noncovalent bonds could be formed when $\gamma$ ceased during the cycle, accompanied by a significant reorganization of the micellar network due to the flow. In addition, short range interactions (electrostatic repulsions of positively charged CTAB headgroups, local frictions between micelles from the extra tail) between adjacent micelles could induce nonlinear stresses at large amplitude of strain, where rearrangements of $\pi-\pi$, cation–π bonds all played important roles in short range interactions, generating “sticky” bumps observed in the stress curve. These short-range interactions between micelles that periodically decomposed and

\[ \gamma = 10\% \sin(\omega t) \quad \text{Wi} = 0.6 \]

\[ \gamma = 50\% \sin(\omega t) \quad \text{Wi} = 3 \]

\[ \gamma = 100\% \sin(\omega t) \quad \text{Wi} = 6 \]

\[ \gamma = 500\% \sin(\omega t) \quad \text{Wi} = 30 \]

\[ \gamma = 800\% \sin(\omega t) \quad \text{Wi} = 48 \]

FIG. 9. For 75 mM CTAB/SHNC solution at 25°C, $f = 0.01$ Hz, $\omega = 2\pi f$ with De = 6: (a) stress response as a function of time; (b) Lissajous stress curves; and (c) normalized high harmonic Fourier coefficients ($I_3$, $I_5$, and $I_7$) under LAOS.
reformed within the oscillatory cycle played a significant role in the distorted rheological response.

High harmonic Fourier coefficients were calculated at 25°C, shown in Fig. 9(c). Similar to the case at 20°C, the normalized $I_n$ ($n = 3, 5, 7$) increased with increasing strains due to entangled micellar networks, then reached an asymptote at higher strains, potentially caused by the viscous dissipation that smoothed out the nonlinearity. The harmonic coefficients at 25°C were much higher than those at 20°C, implying that short-range electrostatic interactions and thermal agitations between micellar headgroups at higher temperatures played important roles in intensified nonlinearity. It can be inferred from Table III that at lower strain amplitudes, mesh size $\xi_m$ remained unchanged, but the zero shear viscosity $\eta_0$ and relaxation time $\tau_r$ at 25°C were much smaller compared with those of 20°C. Thus, at large strain amplitudes, the micellar networks were easier to disintegrate into smaller clusters with a balance between viscous dissipation and intramolecular interactions during oscillatory cycles.

With increasing temperature at 35°C, stress versus time curves showed a linear viscoelastic response for $\gamma$ between 10% and 100%, followed by the emergence of small plateaus and forward tilted stress at $\gamma = 500\%$ and $\gamma = 800\%$ (see Fig. 10), similar to the stress pattern observed at 25°C with $\phi_3 = 270\°$, which appeared at relatively lower strains (i.e., $\gamma = 50\%$). Since the system at 25 and 35°C exhibited distinct differences from both linear viscoelastic (Fig. 3) and strain sweep [Fig. 7(c)] procedures, we propose that the underlying mechanism for the forward tilted stress observed in stress time curves was different at these two temperatures. At 35°C, deformation time ($1/\omega \sim 100\ s$) was much slower than the stress relaxation time ($\tau_r \sim 3.2\ s$) of the entangled micellar networks ($1/\omega \gg \tau_r$), meaning micellar networks have sufficient time to relax during the

FIG. 10. For 75 mM CTAB/SHNC solution at 35°C, $f = 0.01$ Hz, $\omega = 2\pi f$ with $De = 0.2$: (a) stress response as a function of time; (b) Lissajous stress curves; and (c) normalized high harmonic Fourier coefficients ($I_3$, $I_5$, and $I_7$) under LAOS. Deborah number $De = \lambda \times \omega$, and Weissenberg number $Wi = \gamma \times De$. 
oscillation cycle. Clusters of micelles at large strain $\gamma$ can then interact and break into small clusters at the maximum $\gamma$ and reform continuously when $\gamma$ was reversed, which corresponded to the stress bump observed in the stress curve periodically (see Fig. 10). In addition, small stress plateaus accompanied by the development of stress bumps were observed at 35 °C, under $\gamma = 500\%$ and $\gamma = 800\%$ (see Fig. 10). This phenomenon is potentially related to “sliding” layers between micelles [Hyun et al. (2006)]: clusters can align and slide between each other under the flow direction before micellar networks break and reform, yielding a small plateau before the appearance of stress bumps. The normalized $I_n (n = 3, 5, 7)$ at 35 °C were also calculated and plotted in Fig. 10(c). There was a monotonic increase in $I_n$ with increasing $\gamma$, indicating an increasing nonlinearity at this temperature, owing to the continuous break and reform of micelle clusters with higher thermal diffusivity. The hydrophobicity of HNC$^-$ ions decreased with elevating temperatures, leading to weakened $\pi$–$\pi$ and cation–$\pi$ bonds. As a result, each extra benzene ring protruded out of micellar headgroups freely, adding frictions and interactions between micelles during flow that led to increased nonlinearity.

We have also conducted some preliminary tests at fixed value $De = 20$ under 20 ($f = 0.01$ Hz), 25 ($f = 0.03$ Hz), and 35 °C ($f = 1$ Hz). The strain amplitudes for the LAOS are applied at $\gamma = 10\%$, 50\%, 100\%, 500\%, and 800\%. Compared with the LAOS results for 20 °C at $De = 20$, the solution did not exhibit a nearly pure elastic response at 25 and 35 °C at low strain amplitudes $\gamma = 10\%$ and 50\%. At higher strains $\gamma = 100\%$, 500\%, 800\%, the viscoelastic response became more evident for all three temperatures, reflected by more elliptical shaped Lissajous curves (see details in the supplementary material). These preliminary results show interesting features that deserve further investigation, which will be the topic of future work.

Dimitriou et al. (2012) used Rheo-PIV (particle image velocimetry) to characterize the velocity profile and shear bands locations of wormlike micellar solution of 100 mM CPyCl and 60 mM NaSal in their LAOS measurements. They observed that the shear bands existed over the full cycle of the oscillation. Shear bands in our study might form and vanish during the LAOS cycle. We are currently working toward developing a Rheo-PIV system and we hope to be able to perform such experiments and report our results in the near future.

4. Comparing LAOS behavior of CTAB/SHNC and CTAB/NaSal solutions

To distinguish the extra benzene ring effect in the CTAB/SHNC solution, we compared LAOS measurements on both CTAB/SHNC and CTAB/NaSal solutions at the same surfactant and salt concentrations ([CTAB] = 75 mM with $R = 0.32$), at 25 °C (see Fig. 11). The CTAB/NaSal solution exhibited less nonlinear viscoelastic response for all $\gamma$ (see Fig. 11), while forward tilted stress was observed for the CTAB/SHNC solution at increasing $\gamma$ (see Fig. 9). The zero shear viscosity and the stress relaxation time were significantly lower for CTAB/NaSal solution when compared with those of CTAB/SHNC system (see Table I). At 25 °C, $\eta_0$ is 2.5 Pa s and $\tau_r$ is 0.21 s for CTAB/NaSal, while $\eta_0$ is 1000 Pa s and $\tau_r$ is 100 s for CTAB/SHNC system, suggesting faster breaking and reforming rates of micelles in CTAB/NaSal solutions. In the CTAB/NaSal system, the stress versus strain curve also exhibits more circular shaped Lissajous plots, with a phase angle close to 90°, corresponding to a more viscous response under the same large strain deformation. The quantitative comparison of the nonlinearity of the two solutions can be highlighted by plotting Fourier spectrums at $\gamma = 500\%$ and 25 °C. Figure 12(a) illustrated the rich nonlinear behavior of CTAB/SHNC solution with relatively high $I_3$, $I_5$, and $I_7$ at the frequency range from 0 to 0.1 Hz. By contrast, the stress response in the CTAB/NaSal solution exhibited vanishing higher harmonic Fourier coefficients [see Fig. 12(b)].
These comparisons demonstrated that the strong hydrotropic salt SHNC with dual benzene rings induced pronounced viscoelasticity when compared to that of CTAB/NaSal solution. The strong hydrophobicity and high surface activity of SHNC molecules can yield stronger noncovalent interactions between adjacent micelles as hydrophobic HNC ions need to be shielded from water to stabilize these micelles. Consequently, domains of $\pi-\pi$ ions are paired and cation–$\pi$ groups are formed between HNC$^-$ ions and adjacent hydrophobic CTAB headgroups, inducing stable and extensible micellar networks that exhibit versatile response under large deformations and temperatures. In particular, for 75 mM CTAB/SHNC solution, micellar network formed with $\pi-\pi$ ions are paired and cation–$\pi$ groups exhibit stability under different temperatures from 20 to 40 $^\circ$C. Despite the increasing diffusion coefficient $D$ at higher temperatures that led to more agitated interactions of micelles, the Arrhenius relationship remained valid.

IV. CONCLUSIONS

We performed both linear and nonlinear rheological characterizations of an aqueous mixture of cationic surfactant CTAB and hydrotropic organic salt SHNC in the
semidilute regime, coupled with DLS measurements. With SHNC as counter ions, domains of \( \pi-\pi \) ions were paired and cation\(\cdots\pi \) groups were formed between HNC\(^-\) ions and adjacent hydrophobic CTAB headgroups, inducing more viscoelastic and stable micellar networks compared with that of the CTAB/NaSal system. By focusing on 75 mM CTAB/SHNC solution, we observed a rich variety of nonlinear rheological behaviors under different deformation histories with temperatures ranging from 20 to 40 \( ^\circ \)C. Since the naphthalene ring can easily form stable noncovalent bonds that arrest micelles under simple shear flows and small deformations [Frounfelker et al. (2008)], when the deformation time is short compared with micelle relaxation time \( \tau_r \), at 20 \( ^\circ \)C, the viscous dissipation is dominant at higher deformation. At 25 \( ^\circ \)C where the two time scales are comparable, yielding like behavior occurs and is accompanied by short range interactions between micelle head groups. At 35 \( ^\circ \)C, when the deformation time is much faster compared with \( \tau_r \), micelle network breaks and recombines at a fast rate and lead to more frequent interactions.

More specifically, for LAOS and shear hysteresis flow measurements of CTAB/SHNC solutions conducted at different temperatures, two important time scales emerged: deformation time scale from the flow procedure and the longest micelle relaxation time as an intrinsic material time scale. At 20 \( ^\circ \)C, micelle network was “soft” (with low harmonic Fourier coefficients) but the rearrangement of micelles was hindered due to the high viscosity of the solution. As a result, the soft gel continued “yielding” and the progressive alignment and stretching during the flow led to strong and heterogeneous localization of stresses in the entangled networks, with relatively high viscous dissipation during the cycle. At 25 and 35 \( ^\circ \)C, while the micelles were shorter and more mobile, a reorganization of entangled networks and short range interactions between adjacent micelles became more dominant. Meanwhile, reformation of new noncovalent bonds occurred during the deformation period since the micelle relaxation time was shorter. Moreover, additional stress relaxation mechanisms such as contour length fluctuations of reptation chains and constraint release from the motion and rearrangement of neighboring chains, might play an important role in the micelle relaxation mechanism [Bhattacharjee et al. (2003); Cates (1987); Graham et al. (2003); Milner et al. (2001)]. In polydispersed wormlike micellar systems, a simple superposition of the Doi-Edwards model for different chain length was proved to be inadequate in describing the relaxation of micelle

![Fourier coefficient spectrum at \( \gamma = 500\% \) under 25 \( ^\circ \)C (a) 75 mM CTAB/SHNC solution and (b) 75 mM CTAB/NaSal solution. The inserted images are plots of stress versus time curve and Lissajous curve at this particular strain and temperature.](image-url)
system [Cates (1987)]. Therefore, other potential relaxation time scales from the length/concentration fluctuation of micelles might also be responsible for the stress response we observed earlier. Investigations of spatial resolution of heterogeneous bands, formation of shear induced structure phase [Ouchi et al. (2006a); Takahashi and Sakata (2011)] and localization of stresses at different deformations by rheo-optics [Ouchi et al. (2006b); Takahashi et al. (2002, 2001)] will be considered in the future work to correlate shear stress and flow-birefringence, and flow instability in the CTAB/SHNC system. Concentration fluctuation and shear induced bond formation should be studied to further explore the transient behavior of highly viscoelastic hydrotropic micellar system.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from the OIST Graduate University with subsidy funding from the Cabinet Office, Government of Japan (AQS and SJH).

References

Abdel-Rahem, R., “The influence of hydrophobic counterion on the phase behavior of ionic surfactants,” Tenside Surfactants Deterg. 42, 95–101 (2005).
Abdel-Rahem, R., “The influence of hydrophobic counterions on micellar growth of ionic surfactants,” Adv. Colloid Interface Sci. 141, 24–36 (2008).
Abdel-Rahem, R., M. Gradzielski, and H. Hoffmann, “A novel viscoelastic system from a cationic surfactant and a hydrophobic counterion,” J. Colloid Interface Sci. 288, 570–582 (2005).
Becu, L., S. Manneville, and A. Colin, “Spatiotemporal dynamics of wormlike micelles under shear,” Phys. Rev. Lett. 93, 018301 (2004).
Berret, J. F., “Transient rheology of wormlike micelles,” Langmuir 13, 2227–2234 (1997).
Berret, J. F., D. C. Roux, and G. Porte, “Isotropic to nematic transition in wormlike micelles under shear,” J. Phys. II 4, 1261–1279 (1994).
Berret, J. F., G. Porte, and J. P. Decruppe, “Inhomogeneous shear rows of wormlike micelles: A master dynamic phase diagram,” Phys. Rev. E 55, 1668–1676 (1997).
Bhattacharjee, P. K., D. A. Nguyen, G. H. McKinley, and T. Sridhar, “Extensional stress growth and stress relaxation in entangled polymer solutions,” J. Rheol. 47, 269–290 (2003).
Bird, R. B., and B. D. Marsh, “Viscoelastic hysteresis. Part I. Model predictions,” Trans. Soc. Rheol. 12, 479–488 (1968).
Blackwell, B. C., and R. H. Ewoldt, “A simple thixotropic viscoelastic constitutive model produces unique signatures in large-amplitude oscillatory shear (LAOS),” J. Non-Newtonian Fluid Mech. 208, 27–41 (2014).
Brackman, J. C., and J. Engberts, “Influence of polymers on the micellization of cetyltrimethylammonium salts,” Langmuir 7, 2097–2102 (1991).
Britton, M. M., and P. T. Callaghan, “Two-phase shear band structures at uniform stress,” Phys. Rev. Lett. 78, 4930–4933 (1997).
Britton, M. M., R. W. Mair, R. K. Lambert, and P. T. Callaghan, “Transition to shear banding in pipe and couette flow of wormlike micellar solutions,” J. Rheol. 43, 897–909 (1999).
Brown, W., K. Johansson, and M. Almgren, “Threadlike micelles from cetyltrimethylammonium bromide in aqueous sodium naphthalenesulfonate solutions studied by static and dynamic light-scattering,” J. Phys. Chem. 93, 5888–5894 (1989).
Buhler, E., C. Oelschlaeger, G. Waton, and S. J. Candau, “Viscoelastic properties of hydrocarbon/fluorocarbon mixed wormlike micelles at high ionic strength,” J. Phys. Chem. B 108, 11236–11243 (2004).
Cappelaere, E., J. F. Berret, J. P. Decruppe, Y. Cressely, and P. Lindner, “Rheology, birefringence, and small-angle neutron scattering in a charged micellar system: Evidence of a shear-induced phase transition,” Phys. Rev. E 56, 1869–1878 (1997).
Cappelaere, E., R. Cressely, and J. R. Decruppe, “Linear and non-linear rheological behaviour of salt-free aqueous CTAB solutions,” Colloids Surf., A 104, 353–374 (1995).
Cardiel, J. J., A. C. Dohnalkova, N. Dubash, Y. Zhao, P. Cheung, and A. Q. Shen, “Microstructure and rheology of a flow-induced structured phase in wormlike micellar solutions,” Proc. Natl. Acad. Sci. U.S.A. 110, E1653–E1660 (2013).

Cardiel, J. J., Y. Zhao, L. Tonggu, L. G. Wang, J. H. Chung, and A. Q. Shen, “Flow-induced immobilization of glucose oxidase in nonionic micellar nanogels for glucose sensing,” Lab Chip 14, 3912–3916 (2014a).

Cardiel, J. J., Y. Zhao, P. De La Iglesia, L. D. Pozzo, and A. Q. Shen, “Turning up the heat on wormlike micelles with a hydrotropic salt in microfluidics,” Soft Matter 10, 9300–9312 (2014b).

Carver, M., T. L. Smith, J. C. Gee, A. Delichere, E. Caponetti, and L. J., Magid, “Tuning of micellar structure and dynamics in aqueous salt-free solutions of cetyltrimethylammonium mono- and dichlorobenzoates,” Langmuir 12, 691–698 (1996).

Cates, M. E., “Reptation of living polymers—dynamics of entangled polymers in the presence of reversible chain-scission reactions,” Macromolecules 20, 2289–2296 (1987).

Cates, M. E., “Nonlinear viscoelasticity of wormlike micelles (and other reversibly breakable polymers),” J. Phys. Chem. 94, 371–375 (1990).

Cates, M. E., and S. J. Candau, “Statics and dynamics of worm-like surfactant micelles,” J. Phys.: Condens. Matter 33, 6869–6892 (1990).

Debbaut, B., and H. Burhin, “Large amplitude oscillatory shear and Fourier-transform rheology for a high-density polyethylene: Experiments and numerical simulation,” J. Rheol. 46, 1155–1176 (2002).

Decruppe, J. P., O. Greffier, S. Manneville, and S. Lerouge, “Local velocity measurements in heterogeneous and time-dependent flows of a micellar solution,” Phys. Rev. E 73, 061509 (2006).

Da Cruz, F., F. Chevoir, D. Bonn, and P. Coussot, “Viscosity bifurcation in granular materials, foams, and emulsions,” Phys. Rev. E 66, 051305 (2002).

Daniel, C., I. W. Hamley, M. Wilhelm, and W. Mingvanish, “Non-linear rheology of a face-centred cubic phase in a diblock copolymer gel,” Rheol. Acta 40, 39–48 (2001).

Dimitriou, C. J., L. Casanellas, T. J. Ober, and G. H. Gareth, “Rheo-PIV of a shear-banding wormlike micellar solution under large amplitude oscillatory shear,” Rheo. Acta 51, 395–411 (2012).

Divoix, T., V. Grenard, and S. Manneville, “Rheological hysteresis in soft glassy materials,” Phys. Rev. Lett. 110, 018304 (2013).

Dodge, J. S., and I. M. Kriger, “Oscillatory shear of nonlinear fluids I. Preliminary investigation,” Trans. Soc. Rheol. 15, 589–601 (1971).

Doi, M., and S. F. Edwards, The Theory of Polymer Dynamics (Clarendon, Oxford, 1986).

Dubash, N., J. Cardiel, P. Cheung, and A. Q. Shen, “A stable flow-induced structured phase in wormlike micellar solutions,” Soft Matter 7, 876–879 (2011).

Dubash, N., P. Cheung, and A. Q. Shen, “Elastic instabilities in a microfluidic cross-slot flow of wormlike micellar solutions,” Soft Matter 8, 5847–5856 (2012).

Ewoldt, R. H., “Defining nonlinear rheological material functions for oscillatory shear,” J. Rheol. 57, 177–195 (2013).

Ewoldt, R. H., A. E. Hosoi, and G. H. McKinley, “New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear,” J. Rheol. 52, 1427–1458 (2008).

Ewoldt, R. H., and N. A. Bharadwaj, “Low-dimensional intrinsic material functions for nonlinear viscoelasticity,” Rheol. Acta 52, 201–219 (2013).

Fardin, M. A., D. Lopez, J. Croso, G. Gregoire, O. Cardoso, G. H. McKinley, and S. Lerouge, “Elastic turbulence in shear banding wormlike micelles,” Phys. Rev. Lett. 104, 178303 (2010).

Fardin, M. A., T. Divoux, M. A. Guedeau-Boudeville, I. Buchet-Maulien, J. Browaeys, G. H. McKinley, S. Manneville, and S. Lerouge, “Shear-banding in surfactant wormlike micelles: Elastic instabilities and wall slip,” Soft Matter 8, 2535–2553 (2012).

Fardin, M. A., T. J. Ober, C. Gay, G. Gregoire, G. H. McKinley, and S. Lerouge, “Criterion for purely elastic Taylor-Couette instability in the flows of shear-banding fluids,” Europhys. Lett. 96, 44004–44006 (2011).

Fielding, S. M., “Complex dynamics of shear banded flows,” Soft Matter 3, 1262–1279 (2007).

Fielding, S. M., and H. J. Wilson, “Shear banding and interfacial instability in planar Poiseuille flow,” J. Non-Newtonian Fluid Mech. 165, 196–202 (2010).
Fischer, P., E. K. Wheeler, and G. G. Fuller, “Shear-banding structure orientated in the vorticity direction observed for equimolar micellar solution,” Rheol. Acta 41, 35–44 (2002).

Frounfelker, B. D., G. C. Kalur, B. H. Cipriano, D. Danino, and S. R. Raghavan, “Persistence of birefringence in sheared solutions of wormlike micelles,” Langmuir 25, 167–172 (2008).

Garg, G., P. A. Hassan, and S. K. Kulshreshtha, “Dynamic light scattering studies of rod-like micelles in dilute and semi-dilute regime,” Colloids Surf., A 275, 161–167 (2006).

Giacomin, A., and J. Dealy, Techniques in Rheological Measurement, edited by A. Collyer (Springer, Dordrecht, Netherlands, 1993), pp. 99–121.

Giacomin, A. J., and J. M. Dealy, Rheological Measurement, edited by A. A. Collyer and D. W. Clegg (Springer, Dordrecht, Netherlands, 1998), pp. 327–356.

Giacomin, A. J., and R. B. Bird, “Normal stress differences in large-amplitude oscillatory shear flow for the corotational “ANSR” model,” Rheol. Acta 50, 741–752 (2011).

Giacomin, A. J., R. B. Bird, L. M. Johnson, and A. W. Mix, “Large-amplitude oscillatory shear flow from the corotational maxwell model,” J. Non-Newtonian Fluid Mech. 166, 1081–1099 (2011).

Graham, R. S., A. E. Likhtman, T. C. B. McLeish, and S. T. Milner, “Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release,” J. Rheol. 47, 1171–1200 (2003).

Grand, C., J. Arrault, and M. Cates, “Slow transients and metastability in wormlike micelle rheology,” J. Phys. II France 7, 1071–1086 (1997).

Granek, R., and M. E. Cates, “Stress relaxation in living polymers: Results from a Poisson renewal model,” J. Chem. Phys. 96, 4758–4767 (1992).

Gravsholt, S., “Viscoelasticity in highly dilute aqueous solutions of pure cationic detergents,” J. Colloid Interface Sci. 57, 575–577 (1976).

Gurnon, A. K., C. R. López-Barrón, A. P. R. Eberle, L. Porcar, and N. J. Wagner, “Spatiotemporal stress and structure evolution in dynamically sheared polymer-like micellar solutions,” Soft Matter 10, 2889–2898 (2014).

Gurnon, A. S., and N. J. Wagner, “Large amplitude oscillatory shear (LAOS) measurements to obtain constitutive equation model parameters: Giesekus model of banding and nonbanding wormlike micelles,” J. Rheol. 56, 333–351 (2012).

Han, Y. X., Y. J. Feng, H. Q. Sun, Z. Q. Li, Y. G. Han, and H. Y. Wang, “Wormlike micelles formed by sodium erucate in the presence of a tetraalkylammonium hydrotrope,” J. Phys. Chem. 115, 6893–6902 (2011).

Hartmann, V., and R. Cressely, “Influence of sodium salicylate on the rheological behaviour of an aqueous CTAB solution,” Colloids Surf., A 121, 151–162 (1997).

Hassan, P. A., B. S. Valaulikar, C. Manohar, F. Kern, L. Bourdieu, and S. J. Candau, “Vesicle to micelle transition: Rheological investigations,” Langmuir 12, 4350–4357 (1996).

Hatzopoulos, M. H., J. Eastoe, P. J. Dowding, S. E. Rogers, R. Heenan, and R. Dyer, “Are hydrotropes distinct from surfactants?,” Langmuir 27, 12346–12353 (2011).

Helgeson, M. E., D. Reichert, Y. T. Hu, and N. J. Wagner, “Relating shear banding, structure, and phase behavior in wormlike micellar solutions,” Soft Matter 5, 3858–3869 (2009a).

Helgeson, M. E., P. A. Vasquez, E. W. Kaler, and N. J. Wagner, “Rheology and spatially resolved structure of cetyltrimethylammonium bromide wormlike micelles through the shear banding transition,” J. Rheol. 53, 727–756 (2009b).

Hodgson, T. K., and E. W. Kaler, “Hydrotropic solutions,” Curr. Opin. Colloid Interface Sci. 12, 121–128 (2007).

Hoffmann, H., H. Löbl, H. Rehage, and I. Wunderlich, “Rheology of surfactant solutions,” Tenside Deterg. 22, 290–298 (1985).

Holmes, W. M., M. R. Lopez-Gonzalez, and P. T. Callaghan, “Shear-induced constraint to amphipile chain dynamics in wormlike micelles,” Europhys. Lett. 66, 132–138 (2004).

Horbaschek, K., H. Hoffmann, and C. Thunig, “Formation and properties of lamellar phases in systems of cationic surfactants and hydroxy-naphthoate,” J. Colloid Interface Sci. 206, 439–456 (1998).

Hu, Y., C. Palla, and A. Lips, “Comparison between shear banding and shear thinning in entangled micellar solutions,” J. Rheol. 52, 379–400 (2008).

Hu, Y. T., and A. Lips, “Kinetics and mechanism of shear banding in an entangled micellar solution,” J. Rheol. 49, 1001–1027 (2005).
Hyun, K., J. Nam, M. Wilhelm, K. Ahn, and S. Lee, “Large amplitude oscillatory shear behavior of PEO-PPO-PEO triblock copolymer solutions,” Rheol. Acta 45, 239–249 (2006).

Hyun, K., M. Wilhelm, C. O. Klein, K. S. Cho, J. G. Nam, K. H. Ahn, S. J. Lee, R. H. Ewoldt, and G. H. McKinley, “A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS),” Prog. Polym. Sci. 36, 1697–1753 (2011).

Hyun, K., S. H. Kim, K. H. Ahn, and S. J. Lee, “Large amplitude oscillatory shear as a way to classify the complex fluids,” J. Non-Newtonian Fluid Mech. 107, 51–65 (2002).

Ianniruberto, G., and G. Marrucci, “A multimode CCR model for entangled polymers with chain stretch,” J. Non-Newtonian Fluid Mech. 102, 383–395 (2002).

Israelachvili, J. N., Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems (Academic, London, 1985).

Kaler, E. W., A. K. Murthy, B. E. Rodriguez, and J. A. N. Zasadzinski, “Spontaneous vesicle formation in aqueous mixtures of single-tailed surfactants,” Science 245, 1371–1374 (1989).

Kalur, G. C., B. D. Frounfelker, B. H. Cipriano, A. I. Norman, and S. R. Raghavan, “Viscosity increase with temperature in cationic surfactant solutions due to the growth of wormlike micelles,” Langmuir 21, 10998–11004 (2005).

Khatory, A., F. Lequeux, F. Kern, and S. J. Candau, “Linear and nonlinear viscoelasticity of semidilute solutions of wormlike micelles at high salt content,” Langmuir 9, 1456–1464 (1993).

Kim, W. J., and S. M. Yang, “Effects of sodium salicylate on the microstructure of an aqueous micellar solution and its rheological responses,” J. Colloid Interface Sci. 232, 225–234 (2000).

Koppel, D. E., “Analysis of macromolecular polydispersity in intensity correlation spectroscopy: The method of cumulants,” J. Chem. Phys. 57, 4814–4820 (1972).

Krishnaswamy, R., S. K. Ghosh, S. Lakshmanan, V. A. Raghunathan, and A. K. Sood, “Phase behavior of concentrated aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium hydroxy naphthoate (SHN),” Langmuir 21, 10439–10443 (2005).

Lee, J. Y., G. G. Fuller, N. E. Hudson, and X. F. Yuan, “Investigation of shear-banding structure in wormlike micellar solution by point-wise flow-induced birefringence measurements,” J. Rheol. 49, 537–550 (2005).

Lerouge, S., and J. F. Berret, “Shear-induced transitions and instabilities in surfactant wormlike micelles,” Adv. Polym. Sci. 230, 1–71 (2010).

Lerouge, S., J. P. Decruppe, and C. Humbert, “Shear banding in a micellar solution under transient flow,” Phys. Rev. Lett. 81, 5457–5460 (1998).

Lerouge, S., M. A. Fardin, M. Argentina, G. Gregoire, and O. Cardoso, “Interface dynamics in shear-banding flow of giant micelles,” Soft Mater 4, 1808–1819 (2008).

Liberatore, M. W., F. Nettesheim, N. J. Wagner, and L. Porcar, “Spatially resolved small-angle neutron scattering in the 1-2 plane: A study of shear-induced phase-separating wormlike micelles,” Phys. Rev. E 73, 020504 (2006).

Liberatore, M. W., F. Nettesheim, P. A. Vasquez, M. E. Helgeson, N. J. Wagner, E. W. Kaler, L. P. Cook, L. Porcar, and Y. T. Hu, “Microstructure and shear rheology of entangled wormlike micelles in solution,” J. Rheol. 53, 441–458 (2009).

Lin, Y. Y., Y. Qiao, X. H. Cheng, Y. Yan, Z. B. Li, and J. B. Huang, “Hydrotropic salt promotes anionic surfactant self-assembly into vesicles and ultralong fibers,” J. Colloid Interface Sci. 369, 238–244 (2012).

Lu, D. L., J. Cardiel, G. Z. Cao, and A. Q. Shen, “Nanoporous scaffold with immobilized enzymes during flow-induced gelation for sensitive H₂O₂ biosensing,” Adv. Mater. 22, 2809–2813 (2010).

Lu, Y. Y., L. J. An, S. Q. Wang, and Z. G. Wang, “Origin of stress overshoot during startup shear of entangled polymer melts,” ACS Macro Lett. 3, 569–573 (2014).

Manneville, S., L. Becu, and A. Collin, “High-frequency ultrasonic speckle velocimetry in sheared complex fluids,” Eur. Phys. J. Appl. Phys. 28, 361–37373 (2004).

Manohar, C., U. R. K. Rao, B. S. Valaulikar, and R. M. Iyer, “On the origin of viscoelasticity in micellar solutions of cetyltrimethylammonium bromide and sodium salicylate,” J. Chem. Soc. Chem. Commun. 5, 379–381 (1986).

Martineti, L., A. M. Mannion, W. E. Voje, R. X. Xie, R. H. Ewoldt, L. D. Morge, F. S. Bates, and C. W. Macosko, “A critical gel fluid with high extensibility: The rheology of chewing gum,” J. Rheol. 58, 821–838 (2014).
Mendes, E., J. Narayanan, R. Oda, F. Kern, S. J. Candau, and C. Manohar, “Shear-induced vesicle to wormlike micelle transition,” *J. Phys. Chem. B* **101**, 2256–2258 (1997).

Mendes, E., R. Oda, C. Manohar, and J. Narayanan, “A small-angle neutron scattering study of a shear-induced vesicle to micelle transition in surfactant mixtures,” *J. Phys. Chem. B* **102**, 338–343 (1998).

Mewis, J., and N. J. Wagner, “Thixotropy,” *Adv. Colloid Interface Sci.* **147**, 214–227 (2009).

Miller, E., and J. P. Rothstein, “Transient evolution of shear-banding wormlike micellar solutions,” *J. Non-Newtonian Fluid Mech.* **143**, 22–37 (2007).

Milner, S. T., and T. C. B. McLeish, “Reptation and contour length fluctuations in melts of linear polymers,” *Phys. Rev. Lett.* **81**, 725–728 (1998).

Mishra, B. K., S. D. Samant, P. Pradhan, S. B. Mishra, and C. Manohar, “A new strongly flow birefringent surfactant system,” *Langmuir* **9**, 894–898 (1993a).

Mishra, S., B. K. Mishra, S. D. Samant, J. Narayanan, and C. Manohar, “Charge-induced nematic-isotropic transition in mixed surfactant solutions,” *Langmuir* **9**, 2804–2807 (1993b).

Moorcroft, R. L., and S. M. Fielding, “Shear banding in time-dependent flows of polymers and wormlike micelles,” *J. Rheol.* **58**, 103–147 (2014).

Neidhöfer, T., M. Wilhelm, and B. Debbaut, “Fourier-transform rheology experiments and finite-element simulations on linear polystyrene solutions,” *J. Rheol.* **47**, 1351–1371 (2003).

Nemoto, N., and M. Kuwahara, “Dynamic light scattering of CTAB/sodium salicylate long threadlike micelles in the semidilute regime: Applicability of the dynamic scaling law,” *Langmuir* **9**, 419–423 (1993).

Nemoto, N., and M. Kuwahara, “Self diffusion and viscoelasticity of elongated micelles from cetyltrimethylammonium bromide in aqueous sodium salicylate solution. II. Temperature effect,” *Colloid. Polym. Sci.* **272**, 846–854 (1994).

Nemoto, N., M. Kuwahara, M. L. Yao, and K. Osaki, “Dynamic light scattering of CTAB/NaSal threadlike micelles in a semidilute regime. 3. Dynamic coupling between concentration fluctuation and stress,” *Langmuir* **11**, 30–36 (1995).

Oelschlaeger, C., G. Waton, and S. J. Candau, “Rheological behavior of locally cylindrical micelles in relation to their overall morphology,” *Langmuir* **19**, 10495–10500 (2003).

Oelschlaeger, C., P. Suwita, and N. Willenbacher, “Effect of counterion binding efficiency on structure and dynamics of wormlike micelles,” *Langmuir* **26**, 7045–7053 (2010).

Ohlendorf, D., W. Interthal, and H. Hoffmann, “Surfactant systems for drag reduction: Physico-chemical properties and rheological behaviour,” *Rheol. Acta* **25**, 468–486 (1986).

Ouchi, M., T. Takahashi, and M. Shirakashi, “Flow-induced structure change and flow-instability of CTAB/NaSal aqueous solution in a two-dimensional abrupt contract channel,” *Nihon Reoroji Gakkaishi* **34**, 229–234 (2006a).

Ouchi, M., T. Takahashi, and M. Shirakashi, “Shear-induced structure change and flow-instability in start-up couette flow of aqueous, wormlike micelle solution,” *J. Rheol.* **50**, 341–352 (2006b).

Ouchi, M., T. Takahashi, and M. Shirakashi, “Rheological properties of shear-induced structure in CTAB/NaSal aqueous solution—viscosity and elasticity change under start-up flows,” *Nihon Reoroji Gakkaishi* **35**, 107–114 (2007).

Provencher, S. W., “An eigenfunction expansion method for the analysis of exponential decay curves,” *J. Chem. Phys.* **64**, 2772–2777 (1976a).

Provencher, S. W., “A Fourier method for the analysis of exponential decay curves,” *Biophys. J.* **16**, 27–29 (1976b).

Rao, U. R. K., C. Manohar, B. S. Valaulikar, and R. M. Iyer, “Micellar chain model for the origin of the viscoelasticity in dilute surfactant solutions,” *J. Phys. Chem.* **91**, 3286–3291 (1987).

Rehage, H., and H. Hoffmann, “Rheological properties of viscoelastic surfactant systems,” *J. Phys. Chem.* **92**, 4712–4719 (1988a).

Rehage, H., and H. Hoffmann, “Viscoelastic surfactant solutions-model system for rheological research,” *Mol. Phys.* **74**, 933–973 (1991).

Rogers, S. A., “A sequence of physical processes determined and quantified in LAOS: An instantaneous local 2d/3d approach,” *J. Rheol.* **56**, 1129–1151 (2012).

Rogers, S. A., B. M. Erwin, D. Vlassopoulos, and M. Cloître, “A sequence of physical processes determined and quantified in LAOS: Application to a yield stress fluid,” *J. Rheol.* **55**, 435–458 (2011).
WORMLIKE MICELLES WITH HYDROTROPIC SALTS

Rogers, S. A., and M. P. Lettinga, “A sequence of physical processes determined and quantified in large-amplitude oscillatory shear (LAOS): Application to theoretical nonlinear models,” J. Rheol. 56, 1–25 (2012).

Salmon, J. B., A. Colin, S. Manneville, and F. Molino, “Velocity profiles in shear-banding wormlike micelles,” Phys. Rev. Lett. 90, 228303 (2003).

Schubert, B. A., E. W. Kaler, and N. J. Wagner, “The Microstructure and rheology of mixed cationic/anionic wormlike micelles,” Langmuir 19, 4079–4089 (2003).

Shikata, T., H. Hirata, and T. Kotaka, “Micelle formation of detergent molecules in aqueous media: Viscoelastic properties of aqueous cetyltrimethylammonium bromide solutions,” Langmuir 3, 1081–1086 (1987).

Shikata, T., H. Hirata, and T. Kotaka, “Micelle formation of detergent molecules in aqueous media. 2. Role of free salicylate ions on viscoelastic properties of aqueous cetyltrimethylammonium bromide-sodium salicylate solutions,” Langmuir 4, 354–359 (1988a).

Shikata, T., and T. Kotaka, “Entanglement network of thread-like micelles of a cationic detergent,” J. Non-Cryst. Solids 131–133, 831–835 (1991).

Soltero, J. F. A., J. E. Puig, and O. Manero, “Rheology of the cetyltrimethylammonium tosilatewater system. 2. Linear viscoelastic regime,” Langmuir 12, 2654–2662 (1996).

Stepanek, P., J. Jakes, C. Konak, R. Johnsen, and W. Brown, “Dynamic light scattering measurements on the polystyrene/ethyl acetate system at semi-dilute concentrations as a function of temperature,” Polym. Bull. 18, 175–182 (1987).

Subramanian, D., C. T. Boughter, J. B. Klauda, B. Hammouda, and M. A. Anisimov, “Mesoscale inhomogeneities in aqueous solutions of small amphiphilic molecules,” Faraday Discuss. 167, 217–238 (2013).

Takahashi, T., and D. Sakata, “Flow-induced structure change of CTAB/NaSal aqueous solutions in step planar elongation flow,” J. Rheol. 55, 225–240 (2011).

Takahashi, T., H. Sugata, and M. Shirakashi, “Rheo-optic behavior of wormlike micelles under a shear-induced structure formational condition: Verification of stress-optic rule component measurement of refractive index tensor,” Nihon Reoroji Gakkaishi 30, 109–113 (2002).

Takahashi, T., N. Yako, and M. Shirakashi, “Relationship between shear-induced structure and optical anisotropy on cpycl/nasal aqueous solutions,” Nihon Reoroji Gakkaishi 29, 27–32 (2001).

Tapadia, P., and S. Q. Wang, “Nonlinear flow behavior of entangled polymer solutions: Yield like entanglement-disentanglement transition,” Macromolecules 37, 9083–9095 (2004).

Tapadia, P., and S. Q. Wang, “Direct visualization of continuous simple shear in non-Newtonian polymeric fluids,” Phys. Rev. Lett. 96, 016001 (2006).

Vasudevan, M., A. Q. Shen, B. Khomami, and R. Sureshkumar, “Self-similar shear thickening behavior in CTAB/NaSal surfactant solutions,” J. Rheol. 52, 527–550 (2008).

Vasudevan, M., E. Buse, D. Lu, H. Krishna, R. Kalyanaraman, A. Q. Shen, B. Khomami, and R. Sureshkumar, “Irreversible nanogel formation in surfactant solutions by microporous flow,” Nat. Mater. 9, 436–441 (2010).

Verma, G., V. K. Aswal, G. Fritz-Popovski, C. P. Shah, M. Kumar, and P. A. Hassan, “Dilution induced thickening in hydrotrope-rich rod-like micelles,” J. Colloid Interface Sci. 359, 163–170 (2011).

Wang, S. Q., Y. Y. Wang, S. W. Cheng, X. Li, X. Y. Zhu, and H. Sun, “New experiments for improved theoretical description of nonlinear rheology of entangled polymers,” Macromolecules 46, 3147–3159 (2013).

Wilhelm, M., “Fourier-transform rheology,” Macromol. Mater. Eng. 287, 83–105 (2002).

Yin, H. Q., Y. Y. Lin, and J. B. Huang, “Microstructures and rheological dynamics of viscoelastic solutions in a catanionic surfactant system,” J. Colloid Interface Sci. 338, 177–183 (2009).

Yoon, C. J., S. D. Heister, and O. H. Campanella, “Modeling gelled fluid flow with thixotropy and rheological hysteresis effects,” Fuel 128, 467–475 (2014).

See supplementary material at http://dx.doi.org/10.1122/1.4928454 for verification of the rheometer performance at low shear rates. A single mode Maxwell model fit for oscillatory test was provided for 40 mM SHNC/CTAB solution. For 75 mM SHNC/CTAB solution, we conducted additional rheological characterizations: (a) small-angle light scattering (SALS) under transient shear flow; (b) shear hysteresis with rough geometry and down-up versus up-down procedures; (c) large amplitude oscillatory tests (LAOS) at constant De = 20, at temperatures of 20 °C, 25 °C, and 35 °C.