Rheology of Wormlike Micellar Gels Formed By Long-Chained Zwitterionic Surfactants

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Long-chained surfactant solutions have found widespread use in the oil and gas industry due to a host of attractive properties. In this paper, we characterize one such commercially used viscoelastic surfactant that forms a wormlike micellar gel at room temperature and a viscoelastic solution at higher temperatures. We probe both states by conducting linear and nonlinear rheological tests and analyze their behaviour under the framework of micellar rheology. Our study outlines departure from behaviour exhibited by more conventional micellar systems and uncovers interesting dynamics like shear-induced fracture and possible shear-banding in these materials. In doing so we provide a detailed understanding of a novel class of wormlike micellar solutions.

I. INTRODUCTION

The amphiphilic nature of surfactant molecules leads to unfavourable contact between its hydrophobic tail section and the solvent, resulting in a wide variety of spontaneous self assembled structures. The morphology of these assemblies is dictated by energetic and entropic considerations and is a complex interplay of geometry and physiochemical interactions which can be controlled by a gamut of parameters like temperature, surfactant concentration, solvent pH and added molecules (salts, co-surfactants etc). Increasing surfactant concentration favours the formation of linear wormlike chains which can entangle to form a dynamic network of wormlike micelles (WLM). Further increasing surfactant concentration can lead to the formation of a network of branched micelles. For this paper, our system of investigation comprises of aqueous solutions of entangled WLM’s.

The study of micellar solutions as complex fluids has been an active field of research for a long time owing to interesting flow dynamics [1] and rheology [2, 3]. While, at a static coarse-grained level, entangled WLM solutions share similarities with entangled polymer suspensions, there are two crucial differences. The contour length of worms in WLM solutions is not fixed and has a broad distribution that depends on external factors like temperature [4]. Also, unlike polymers, surfactant worms are held together by non-covalent bonds. These weak bonds allow frequent monomer exchange between worms - a breaking-recombination process that leads to the formation of a transient entangled network and lend worm-like micellar solutions the monicker of living polymers. The dynamic nature of micellar networks allows the complex fluid to have an additional mechanism for stress relaxation. Much like a system of entangled polymers, entangled worms can relax stress by reptation - diffusing out of surrounding constraints. But, while the worms reptate out of their confining tube, they can break and recombine multiple times. In the fast breaking limit, the solution is a viscoelastic liquid with a single relaxation time [5]. This property makes WLM solutions a fertile system for experimental and theoretical investigation as they can also be used as a proxy for viscoelastic fluids with Maxwellian rheology. Additionally, WLM solutions re-form after shearing unlike polymer solutions that degrade permanently when exposed to strong shear flows. WLM solutions thus prove to be ideal systems to probe nonlinear flow and rheological behaviour [2, 4]. Entangled WLM solutions, often in the semi dilute regime, display a host of instabilities in different canonical fluid flow scenarios [7, 9]. Understanding the genesis of these novel dynamical phenomena and tying them to microstructural details is a major challenge in complex fluid dynamics and rheology [1] [10].

Aside from being interesting from a fundamental perspective, WLM solutions are crucial in a number of industrial applications [11]. Properties that make them attractive rheology modifiers include high shear rheology, viscoelasticity and self-healing ability. A combination of these properties are often exploited in biomedical, pharmaceutical and personal health applications. But perhaps the most active use of WLM solutions has been in the oil-gas industry [12]. WLM solutions can suspend particles due to their high viscosity, but do not incur energy penalties while pumping owing to viscoelasticity enabled drag reduction capabilities. Drag reduction in viscoelastic fluids is a research problem of immense interest in physics and engineering [13]. While, extensively investigated in polymeric fluid systems [14], drag reduction by surfactant additives has also gained attention [15]. Here too, there is a strong demand for a fundamental understanding of the rheology WLM solutions.

In the last two decades, a specific type of surfactant based fluid has stoked the interest of rheologists, primarily motivated by hydraulic fracturing [16] and gravel packing operations [17] in oil and gas production. In the former, a carrier fluid drives the suspended proppant particles to fill fractures in bedrock. In the latter, gravel carried by a suspending fluid is used to ‘pack’ behind wellbore screens and prevent sand contamination. Both processes utilize the above mentioned beneficial properties of WLM solutions, namely excellent solid
Rheology of Wormlike Micellar Gels

Long-chained surfactants have tails of 12, 16 or 18 carbon atoms and is thus referred to as long-chained. The first such WLM solution studied was EHAC and it showed some rheological oddities [20]. The WLM solution behaved like an elastic gel at room temperature, a marked difference from conventional WLM rheology which typically displays Maxwellian viscoelasticity. Studies on long-chained surfactant systems have since then been pioneered by Raghavan [20, 21], Feng and co-workers [22–24]. In [21], a detailed rheological study of a long-chained (22 C atoms) zwitterionic surfactant system called EDAB unveiled gel-like rheology and a yield stress at room temperature. Solutions of EDAB reverted to classical Maxwellian rheology at higher temperatures i.e WLM solutions of EDAB showed a elastic gel-viscoelastic sol transition with temperature. The gel-like nature of these solutions is antithetical to traditional WLM solutions and is thought to arise from purely topological interactions [25, 26].

Because of the wide-ranging usage of wormlike micellar solutions, there is a consistent push for the design of smart micelles that can respond actively/passively to various stimuli [27]. In this context, surfactant gels are increasingly being considered as a viable replacement for polymer based hydro-gels in biomedical applications like tissue engineering [28]. Further, researchers have proposed [25, 29] that gel formation in surfactant systems shares similarities with some molecular self-assembled systems like entangled F-Actin [30]. In fact, strain stiffening, a signature of many biopolymer networks was also observed in a surfactant based organo-gel [31]. Certain dendritic surfactant systems [32] have utility in the fabrication of nanomaterials. Recently, one such system was shown to exhibit structural and rheological properties of gels formed by entangled wormlike micelles [33]. Thus, wormlike micellar gels are not only an interesting soft matter system by themselves, but can prove to be a fertile experimental playground to understand behaviour of many analogous systems too. A prime goal of this study is to properly investigate the linear and nonlinear rheology of wormlike micellar gels formed by long chained zwitterionic surfactants and place this unique surfactant system, first within the narrow context of wormlike micellar solutions and then in the broader context of gels and amorphous soft matter.

The surfactant system we focus on is a viscoelastic surfactant solution (VES) provided by Schlumberger Oilfield Services. The solution contains a zwitterionic surfactant similar to previously studied systems [21]. Among surfactants, zwitterionic systems are popular in commercial applications as they have environmentally friendly qualities [34] like high biodegradability [35] and minimal toxicity and have yet received only scant interest from academia. The specific VES system was used in [36] in which the authors showed that the VES displayed gel-like behaviour. While [36] primarily focused on shear-rheology in the context of flow-loop studies, here we carry out a more extensive analysis of VES’s rheological behaviour by using oscillatory and shear-rheology probes. We characterize the microstructure visually and then indirectly via rheology based analysis and then move on to discussing dynamics under an imposed shear-rate.

II. MATERIALS AND METHODS

A. Surfactant and Preparation

Our model system is a drag-reducing gravel packing surfactant product called J590 that is supplied to our laboratory by Schlumberger in liquid form [36]. VES solutions are usually a combination of a zwitterionic surfactant and a polar solvent - an alcohol for example. Our VES solutions contain a mixture of erucic amidopropyl dimethyl betaine and propan-2-ol. The surfactant in the VES solution has a CAS number whose associated structure is similar to the zwitterionic surfactants used in previous studies [21, 37]. In [21], the surfactant is called EDAB and [37] refers to it as EAPB. We refrain from calling our surfactant solution either of those two names, and refer to it as VES throughout the paper. However, we expect that our results should be closely related to studies reported on EDAB/EAPB. Further, because the exact percentage of surfactant in the VES is unknown in the commercially supplied product, we only mention concentration (by % weight or volume) of the provided VES solution which is proportional to the true surfactant concentration. We use the VES as supplied. Inorganic salts, if present, have little effect on the rheological behaviour of zwitterionic surfactants [21] and small amounts of alcohol do not greatly affect EDAB’s rheological properties [38]. To prepare the micellar solution, we use tap water as solvent in order to simulate typical working conditions of the fluid in practice more closely and allow compliance with flow studies being conducted currently in our group. A single concentration of VES was mixed with deionized (DI) water and tested at two temperatures and we found no appreciable change in relevant quantities. Concentrations between 1 and 10 % of surfactant was mixed vigorously with an IKA control 60 mixer at 2000 rpm for 20 minutes, with a high shear rate impeller. After mixing, the solution ends up being foamy due to the high mixing speeds. To de-gas the fluid, we can centrifuge at 3000 rpm for 10 minutes and then store the solution in a thermal bath for ~1hr at 80°C. A well mixed solution appears transparent on visual inspection.

B. Methods

Rheological studies were performed with a Malvern Kinexus stress-controlled rheometer in a concentric cylinder geometry with a cup of 37.00 mm diameter and height of 66.00 mm, and bob with 33.65 mm diameter, 37.50 mm height and cone angle of 15°. The inner surface of the cup and the outer surface of
the bob were roughened to prevent wall slip. Prior to beginning experiments, the fluid was left to stabilize at a desired temperature for \( \sim 20 \) minutes. A solvent trap was used to prevent evaporation of the sample. To erase memory of loading and ensure a well defined initial state, we applied a pre-shear at \( 100 \text{ s}^{-1} \) for 6 minutes, followed resting time of 30 minutes at 0 Pa before every experiment. This protocol is critical as the VES solution experiences a growth of elastic modulus \( (G') \) with time, indicating structure buildup after structure destruction due to shearing (as experienced in the loading process).

C. Cryo-TEM

Cryo-TEM was performed in the Life Sciences Institute in the University of British Columbia. Samples of 4.5 % and 10% for cryo-TEM were prepared in a low humidity room to minimise contamination. Before vitrification, excess sample on the grid is removed by blotting, which shears the micellar structure. Keeping this in mind, samples were rested for \( \sim 5 \) minutes after blotting, to allow microstructure to relax after blotting. We cannot guarantee that the chosen resting time between blotting and imaging is "sufficient" to let the microstructure fully relax. However, the waiting time in combination with other factors involved in this technique provided good micrographs. We acknowledge that some images showed a high degree of preferred alignment which is most likely a shear induced artifact. However, we expect that resting time should not affect the general morphology of micelles. The surfactant sample is then quenched very quickly in ethane at -180°C. Visualization of the micellar structure in the vitrified samples was performed with a 300kV FEI Titan Krios electron microscope, equipped with a Falcon III camera.

III. RESULTS

A. Visual Observations

After preparation, the VES solution appears gel-like at room temperature. Bubbles trapped remain so indefinitely and a vial of 10 % solution holds its own weight when upturned for many days (Fig 1(a)). Vials of VES sample show strong birefringence when tilted and viewed in the presence of plane polarized light and a polarizer as seen in Fig 1(b), implying the presence of long structures that align when oriented, presumably micelles. The VES contains a zwitterionic surfactant in which closely situated opposite charges on the headgroup almost cancel each other leading to minimal headgroup repulsion. Such surfactants are therefore expected to form cylindrical wormlike micelles without the addition of salts [21]. That wormlike micelles are indeed present in our VES solutions is confirmed on looking at Cryo-TEM images of our samples. Cryo-TEM is an ideal technique for visually probing complex fluids owing to the method’s ability to directly image material microstructure in a natural state [39]. We image VES samples of two different concentrations (4.5,10%) and show representative images in Fig 2. Cryo-TEM images have low contrast owing to the vitreous ice layer. However, our images are clear enough to confirm that VES samples indeed contain long wormlike/threadlike micelles. It is noteworthy that there are no visible cross-links or branching. The latter manifests as junctions in individual micelle threads that have the same contrast as the original micelle. Instead, we see a network of wormlike micelles in an overlapping - entangled mesh. Points of entanglement can be identified as they appear darker than the rest of the micelle [39, 40]. Quantifying total and persistence lengths from such images is a challenging task that requires analysis of images from a variety of tilt angles [41]. However, we see from Fig 1(a,b) that micelles are long and of O(1\,\mu m). For the 4.5% sample, the worms look rigid and persistent, more so than the micelles in the 10% sample. It is possible that the visible rigidity in the 4.5% sample is due to the straightening of micelles during blotting, whereas the visual difference between the two samples could be a result of difference in their relaxation times. Finally, we note that the images of our VES samples look very similar to those reported for EDAB in [25, 26]. Essentially, our Cryo-TEM images reaffirm that at room temperature, the VES samples contain long and entangled wormlike micelles.
B. Behaviour in Small Amplitude Osculatory Sweep (SAOS) tests

To gain better insight into specifics of the rheological behaviour displayed by VES samples we first perform basic SAOS tests. Typically, entangled wormlike micelles display a classical Maxwellian viscoelastic behaviour in this test. The storage $G'\!$ and loss $G''\!$ moduli crossover at a critical frequency $\omega_0\!$ which demarcates the behaviour of the solution as elastic ($\omega > \omega_0\!$) and viscous ($\omega < \omega_0\!$) and ends it with a single dominant relaxation time $\tau_0 = \omega_0^{-1}\!$. The VES samples at 25°C show a marked deviation from this expected behaviour. As seen in Fig. 3, the storage modulus is independent of $\omega$ for almost 3 decades, with no crossover in the two material moduli for the range of frequencies probed. $G'/G'' > 10\!$, for the range of frequencies probed. Thus, VES samples behave like elastic gels or solids with no structural relaxation at least on experimental timescales probed. This is contrary to conventional entangled wormlike micellar solutions, which may have a tendency to appear gel-like but show clear frequency dependence and crossover for $G', G''\!$.

The gel-like rheology displayed by VES at room temperature is a unique feature shared by long-chained surfactant solutions, previously established for other surfactant systems like EHAC [20] and EDAB [21]. In this, entangled wormlike micellar solutions formed by such surfactants share similarities with other molecular gel systems like F-Actin which can form gels despite the lack of chemical or physical crosslinks [20]. Cross-links or jamming of constituents in classical gel systems constrain relaxation, leading to infinite relaxation times. However, as observed in our Cryo-TEM images, VES samples do not show cross-linking and only contain worms with topological constraints akin to entanglements. In [20], it was proposed that such physical constraints can lead to very long reptation times and in combination with the unfavourable breaking process in worms, explain gel-like rheology in long-chained surfactant systems like the one we employ in this paper. We also notice that, unlike the frequency independence of $G', G''$ seems to display two regimes. For $\omega < 1s^{-1}, G''$ doesn’t vary with $\omega\!$, whereas for $\omega > 1s^{-1}, G'' \sim \omega^{\alpha}$; the exponent $\alpha$ varies with concentration. This kind of power law dependence of loss modulus on frequency is reminiscent of other soft matter systems. For instance, $G'' \sim \omega^{0.5}$ was observed in an emulsion system and interpreted as a dissipative contribution to the loss modulus activated at higher frequencies due to in-plane slip of material regions [42]. A similar trend exists for microgel systems in which $G'' \sim \omega^{\alpha}, \alpha \in (0.3 - 0.5)$ for a range of concentrations [43–45]. Although, these power laws are established for a large range of frequencies starting typically from $\omega > 1s^{-1}$, we were unable to get data for $\omega > 10s^{-1}$ owing to errors induced by instrument inertia. However, our system shows a consistent power law for $1s^{-1} < \omega < 10s^{-1}$ for independent measurements and different concentrations as seen in Fig. 4. It is possible that the mechanism responsible for frequency dependence of $G''$ in microgels and emulsions is active in our wormlike micellar gels too, although the microstructure underlying above mentioned emulsions and microgels bear a stark contrast to entangled wormlike micelles in VES.

Finally, we show the concentration dependence of the plateau modulus, $G_p$ in Fig. 5. $G_p$ is calculated by averaging the elastic modulus over a frequency range of $\omega \in (0.02\pi - 0.2\pi)\!$ radi/second over which the moduli is independent of $\omega\!$. Fitting to a power law results in $G_p \sim \omega^\beta, \beta = 2.28$. It is not straightforward to glean information from the value of $\beta\!$, but we note that it lies in the range of values reported for conventional micellar systems for which the plateau modulus, $G_p$ typically scales with concentration as $G_p \sim c^\beta, \beta \in (1.8 - 2.4)$ [10].

For some systems exhibiting gel-like rheology the large-ness of the exponent can be related to the relative flexibility of
FIG. 5. $G'$ averaged over $\omega \in (0.02\pi - 0.2\pi)$ rad/s and reported as $G_p$ vs surfactant concentration $c$ at 25C. Black line denotes power law fit (straight line in log-log scale).

constituent fibres. For instance, collagen and fibrin hydrogels were shown to have exponents of 2.48 and 1.86 respectively; concurrently fibrin hydrogels had flexible chains compared to the stiffer elements forming collagen networks [46]. We note that physical networks of sterically hindered fibres like our VES systems have been shown to have an exponent of $c^{2.2}$: F-Actin made up of semi-flexible fibres with bending rigidity was predicted to show this exponent [47] and recently the same concentration dependence was found in nanofibrillar networks [48]. In [48], this exponent increased for higher concentrations and the regime in which $G' \sim c^{2.2}$ was primarily a ‘fluid’ regime for which $\tan \delta = G''/G' > 1$. For the VES however, this scaling was observed for a decade in concentrations and the regime in which $G_p$ magnitudes smaller than the reptation time, $\tau_{br}$, is orders of magnitude greater than the reptation time, $\tau_{br}$, for micelles in an entangled network. Here, we note that the VES moduli at 25C did not show terminal behaviour at low frequencies. In particular, the absence of linear dependence of $G''$ with $\omega$, at the lower range of frequencies probed, points to very slow relaxation process more typical of soft glassy matter than wormlike micellar solutions.

We now move on to SAOS tests carried out at 60C. Representative plots for two concentrations are shown in Fig. 6 and we clearly see that VES rheology at this temperature is different from the gel-like rheology displayed in SAOS tests at 25C. Both, $G'$, $G''$ are functions of $\omega$ and the dependence is well captured by the Maxwell-fluid model in which viscoelasticity is idealized by a series connection of spring (viscous) and dashpot (elastic) elements resulting in a viscoelastic fluid with a single relaxation time. The functional dependence of the moduli on frequency predicted by this model are:

$$G' (\omega) = \frac{G_p \omega^2 \tau_r^2}{1 + \omega^2 \tau_r^2} \quad (1)$$

$$G'' (\omega) = \frac{G_p \omega \tau_r}{1 + \omega^2 \tau_r^2} \quad (2)$$

Here, $\tau_r$ is the single relaxation time which is the inverse of the frequency ($\omega_r$) at which $G'$ and $G''$ crossover, signalling a regime shift in the behaviour of the solution, $G_p$, is the value of plateau in the elastic modulus attained at higher frequencies. Both moduli show terminal behaviour at lower frequencies.

These features are typical of entangled wormlike micellar solutions in the linear viscoelastic regime [3]. The adherence to viscoelasticity defined by a single relaxation time is also a marker of the micelles in solution being in the fast breaking limit in which their dynamic breaking time, $\tau_{br}$, is orders of magnitudes smaller than the reptation time, $\tau_{rep}$ for micelles in an entangled network. Here, we note that the VES moduli at 25C did not show terminal behaviour at low frequencies. In particular, the absence of linear dependence of $G''$ with $\omega$, at the lower range of frequencies probed, points to very slow relaxation process more typical of soft glassy matter than wormlike micellar solutions.

A notable feature of SAOS behaviour of VES at 60C is the deviation from predictions of the Maxwell model at higher frequencies which occur due to the dynamic nature of micelles that can break and recombine. While collective network dynamics dominate in the plateau modulus regime, higher frequencies trigger intra-filament modes like bending and Rouse modes which are not accounted for in the Maxwell model [49]. Activation of such relaxation modes leads to an upturn of $G'$, $G''$ at high values of $\omega$, an effect which cannot be fully captured by bulk rheometry owing to instrument inertia limitations and can be captured by microrheology probes [50]. We fit SAOS data at 60C to the Maxwell model (Eq. 12) and extract values of $G_p$ and $\tau_r$ for different surfactant concentrations, $c$. The data also allows us to quantify $\tau_{br}$ which is the breaking and reformation time of micelles in equilibrium. While $\tau_{br}$ can be calculated via different techniques [51], we use the inverse of frequency ($\omega_{min}$) at which $G''$ attains a minimum as an estimate of $\tau_{br}$. $\tau_{br} = 1/\omega_{min}$. $G_p$ follows a power law dependence on concentration, $G_p \sim c^{2.05}$ as seen in Fig. 7, which we note is a weaker dependence than observed at 25C. The reason for this is unclear at this point.

Before we comment on the variation of $\tau_r$, $\tau_{br}$ with $c$ in our system, it is instructive to re-visit what theory predicts for these dependencies in wormlike micellar solutions. The
two processes that control stress relaxation in these systems vary differently with micellar lengths and hence with $c$. If $\tau_{br}$ is taken to be the rate of unimolecular scission occurring randomly at any point along the length of a micellar chain with reaction rate $k$, $\tau_{br} \sim 1/kL$ where $L$ is the average length of a micellar chain \[4\]. A mean-field prediction for reptation time, $\tau_{rep}$ in unbreakable polymers is encapsulated in the relation $\tau_{rep} \sim c^2L^3$ and the mean-field prediction for average chain length dependence on surfactant concentration is $\bar{L} \sim c^{1/2}$ \[52\]. For $\tau_{br} \ll \tau_{rep}$ the single relaxation time, $\tau_r$ is given by $\tau_r = \sqrt{\tau_{rep}\tau_{br}}$ \[5\]. Combining the above mentioned equations gives $\tau_r \sim c^{3/2}$ and $\tau_{br} \sim c^{-1/2}$. In Fig.8 we plot $\tau_{br}, \tau_r$ for different concentrations at 60C and see that while $\tau_{br}$ expectedly decreases with increasing $c$, it is a much sharper decrease than the 1/2 power law exponent predicted by scaling theory. Force fitting the data in Fig.8 gives $\tau_{br} \sim c^{-1.25}$. For $\tau_r$, the trend seen in experiments is opposite to that predicted by scaling theory - $\tau_r$ decreases with $c$ with a possible maximum between 1 – 2%.

The scaling theory is developed for neutral micelles, and it is thus not exceptional that many surfactant systems which might be strongly influenced by added counterions, insufficient screening or structural transitions, do not follow the expected scaling \[52,55\]. However, zwitterionic surfactants are self-screening and are thus expected to be close approximations of neutral micelles in solution. Hence, such a large deviation from theory is surprising. Studies on zwitterionic systems are relatively scarce. While the concentration scaling of shear viscosity has received attention \[22,56,57\], to the best of our knowledge, there aren’t any reports of concentration dependence of $\tau_r, \tau_{br}$ for long-chained zwitterionic surfactants. However, we extracted data from Figure 3,4 in \[21\] for EDAB and found that $\tau_r$ is a decreasing function of $c$ at 60C - a trend in agreement with what is observed for the VES (although the dependence in \[21\] is much weaker than in Fig.8).

This discrepancy in $\tau_r$ vs $c$ data has been ascribed to the presence of micellar branching in systems where the trend followed by $\tau_r$ is mirrored by shear viscosity $\eta = G_p \tau_r$ \[55\]. Here, $\eta$ is an increasing function of $c$ throughout the investigated range (not shown) and the strength of the variation is close to that deduced from data in \[21\]. While we haven’t directly imaged VES at 60C, it is important to note that no sign of branching was observed in Cryo-TEM images at room temperature. Finally, the dependence of plateau modulus, $G_p$ on $c$ in branched systems is usually weaker than what is observed for VES \[22\]. A possible reason for the anomalous variation of $\tau_r$ with $c$ in our VES system could be a deviation in $\bar{L}$’s dependence on $c$ from the $\bar{L} \sim c^{0.5}$ growth law predicted by theory. Both $\tau_{br}$ and $\tau_r$ are functions of $L$ and strongly influenced by how micellar length depends on surfactant concentration. This deviation could be induced owing to subtle dependence on end-cap energy $E_c$ on $c$ \[53\]. $E_c$ sets the favourability of creating two end-caps from none and hence critically decides the length of cylindrical wormlike micelles in solution. We do not investigate this situation further. However, our results call for more experimental and theoretical work on self-assembly in zwitterionic micelles and related systems \[21,58\]. We conclude this discussion on scaling of relevant parameters with surfactant concentration by noting that while the reported scalings for $\tau_r$ and $\tau_{br}$ differ from that predicted by mean-field theory, the plateau modulus scaling is close to the mean-field theory prediction \[59\] and values reported for some smaller chain surfactants (for example in \[60,61\]). We also note that the reported scaling for $\tau_{br}$ is close to the newly uncovered value of -1.1 reported in \[62\] by conducting mesoscopic simulations with the inclusion of fast Rouse modes.

We can extract more information about the microstructure of VES from SAOS tests at 60C. The pore size or mesh spacing $\xi$ is related to the plateau modulus as $G_p = 9.75 \xi^2 kT$ \[62,63\]. Plugging in the values of $G_p$ for $c = 4.5\%$ we get $\xi \approx 179$ nm. The value of $\xi$ is typically independent of temperature and we expect that these mesh gaps characterize the entangled micellar network throughout this high temperature range. To get an idea of other length scales that describe the
entangled wormlike microstructure, we require an estimate of persistence length \( l_p \). Persistence length is a difficult quantity to measure and is performed either by sophisticated scattering techniques \([37]\) or high-frequency rheology \([64]\). To the best of our knowledge, the only \( l_p \) measurement for a zwitterionic long-chained surfactant system was carried out in \([37]\).

For a 2% EAPB system, the value reported was \( \approx 150 \text{ nm} \), a value much higher than \( l_p \) for conventional micellar systems which are influenced by salt content and lies between 30-60 nm. Assuming \( l_p \) is unaffected by temperature, we use this value as an estimate for \( l_p \) for 4.5% VES at 60C. For \( \xi \approx 83.6 \text{ nm} \) and \( \xi = \frac{l_p^{1/3}}{l_c^{1/3}} \) \([49]\) we get \( l_c \approx 200 \text{ nm} \) : \( l_c \) is the length of micellar sections between points of entanglements. To get \( \bar{L} \) we use the formula - \( G_p/G_{\min}^{''} \approx 0.317(\bar{L}/l_c)^{0.82} \) \([62]\). The values of \( G_p/G_{\min}^{''} \) at 60C decrease with \( c \) and for 4.5% VES solution is \( \approx 0.024 \) which gives approximately 188 entanglements points per chain length and a value of \( \bar{L} \approx 33 \mu \text{m} \). While, this value of \( \bar{L} \) seems exceedingly large for micelles at 60C, we note that it lies close to the range reported for micelles formed by cationic long chained surfactants \([20]\) and calculated for zwitterionic long-chained surfactants - EDAB \([21]\), provided the updated formulæ from \([62]\) are employed. Long wormlike micelles imply very long \( \tau_{rep} \), which satisfies one of the conditions that allow for the gel-like rheology at room temperatures, the other being large values of \( \tau_{br} \).

We carry out SAOS tests at temperatures between 60 and 80C for 4.5% VES. Slight changes in \( G_p \) can be accounted for by plateau moduli’s linear dependence on \( T \). This validates our assumption of temperature independence of \( \xi, l_c, l_p \) at these temperatures. We also find that \( \tau_r, \tau_{br}, G_p/G_{\min}^{''} \) can be fit by a straight line in a semi-log plot, indicating an Arrenhius type variation for these quantities as seen in Fig. \([9]\) From the Arrenhius variation \( \tau_r \sim e^{E_{esciss}/k_bT} \), we obtain the flow activation energy, \( E_r \). Our data gives \( E_r \approx 61 k_bT \) or 152 kJ/mol, close to the value obtained for EDAB in \([21, 57]\).

The decrease of relaxation time with increasing \( T \) is mediated via (1) - drastic reduction in reptation time due to exponentially decreasing mean micellar length and (2) - decreasing breaking time with \( T \) as seen in Fig. \([9]\). As \( G_p^{''}/G_{\min}^{''} \approx l_c/\bar{L} \) and \( l_c \) is constant in this range of \( T \), a reduction in \( \bar{L} \) implies an increase in the value \( G_p^{''}/G_{\min}^{''} \): a decrease in \( \tau_{br} \) with increasing \( T \) also pushes the minimum in \( G_p^{''} \) to higher frequencies as seen in Fig. \([10]\). The reductions in both \( \bar{L} \) and \( \tau_{br} \) are mediated by activation energies: \( \bar{L} \sim e^{E_{esciss}/k_bT} \) and \( \tau_{br} \sim e^{E_b/k_bT} \), where \( E_b \) is the activation energy required for breaking a micelle and \( E_{esciss} \) is the scission energy. For nonionic micelles, \( E_{esciss} \approx E_c \) so we expect that for zwitterionic surfactants, \( E_{esciss} \) is very close to the end-cap energy. The Arrenhius fits for \( G_p/G_{\min}^{''} \) and \( \tau_{br} \) give values \( E_c \approx 51.2 k_bT \) and \( E_b \approx 28 k_bT \). To the best of our knowledge, these are the first values reported for long-chained zwitterionic surfactant systems. They compare favourably to those extracted from Fig.3 in \([21]\) for EDAB: \( E_c \approx 53.6 k_bT \) and \( E_b \approx 28 k_bT \). However, they are much lower than those in \([20]\), where the authors reported (note that authors in \([20]\) have used \( G_p/G_{\min}^{''} \sim (\bar{L}/l_c) \) instead of \( G_p/G_{\min}^{''} \sim (L/l_c)^{0.82} \) an unusually high value (65\( k_bT \)) of \( E_{esciss} \) for long-chained cationic surfactant - EHAC. This was interpreted in the context of the larger lengths of micelles formed by long-chained surfactants, and later aiding the hypothesis for long breaking times of C22-tailed surfactants \([21]\). We expected the VES and EDAB, both characterized by long carbon chains, to have activation energies similar to that reported in \([20]\). Clearly, this is not the case. How do we rationalize this discrepancy in scission energies?

The formula \( \bar{L} \sim e^{E_{esciss}/k_bT} \) from Cates theory does not account for entropic contributions to \( E_{esciss} \) \([4]\) and it was suggested that the values of activation energy calculated from Arrenhius fits only yield the enthalpy of scission, \( H_{sciss} \), rewriting \( E_{esciss} = k_bT S_{sciss} \), where \( S_{sciss} \) is the entropy of scission \([65, 66]\). The system employed in \([20]\) consists of a low ionic strength surfactant in conjunction with Salycitate counterions from the
salt used. This is likely to lead to the very high values of $H_{\text{sciss}}$ and a positive $s_{\text{sciss}}$ can then lead to lower values of $E_{\text{sciss}}$, closer to the ones we report here for the VES and EDAB in [21]. We note that zwitterionic surfactants should mimic well screened systems and as such, values calculated here and from [21] should closely relate to those reported in [65] where the authors employed a highly screened surfactant system. This is not the case and it indicates that it is likely that $H_{\text{sciss}} \approx E_{\text{sciss}}$ for VES and EDAB, unlike the system employed in [65]. It remains to be established if positive entropic contributions can further reduce enthalpies to even lower values. To better answer the hypothesis of very large breaking times, pin-point its origin, and connection to scission energies, measurements of $\tau_{\text{br}}$ at lower temperatures along with energetic and entropic calculations of micellar formation and breaking process are needed. These remain out of the scope of the present study. Finally, we see that the value of $G_p$ changes with $T$ in an interesting fashion as seen in the inset of Fig. 11. From 25-60°C there is a steeper increase followed by small increments past 60°C which, as mentioned previously, can be accounted for by the $G_p$'s linear dependence of $T$ in that regime. The steeper increase is hypothesized to be caused by a temperature driven increase in effective surfactant concentration which results from solubilization of molecules at higher $T$ [20, 57]. Thus the gel-sol transition in these systems in driven by an increase in temperature and plateau modulus. Two dominating factors govern this transition induced by temperature - (1): Reduction in micellar mean length that leads to drastic reduction in reptation times, (2): Reduction of breaking times. Both these factors push the WLM system to the fast breaking limit. A balance of these two opposing effects dictates if micellar gels do not maintain this balance as is also evident from the lack of shear-thickening in imposed shear-rate tests. A balance of these two opposing effects dictates if entangled micellar networks stiffen or soften under increasing deformation amplitude. It is likely that our wormlike micellar gels do not maintain this balance as is also evident from the lack of shear-thickening in imposed shear-rate tests. Note, shear-thickening was an accompanying response observed in strain-stiffening reverse micelle networks. If this mechanism for strain-stiffening proposed by [68] holds, it should, in principle, be possible to engineer micellar gels with strain-stiffening properties by precisely tuning polydispersity and persistence length. Another detail is the increase in $G''$ with $\gamma^\%$ in the nonlinear regime for the 8% VES. Before we discuss this further, it is imperative to mention that data in the nonlinear regime is not drawn from steady state responses and as such the values of $G''$ at amplitudes in that regime might change if we wait for long enough time to achieve steadiness. However, we expect that the presence of an overshoot should not be affected.

C. Behaviour in Strain Amplitude Sweep

The issue of strain-stiffening has been a subject of intense discussion, mostly in the context of biopolymer solutions and gels that are generally characterized by permanent networks comprising of semi-flexible fibres [57]. In a strain-amplitude sweep test, strain-stiffening manifests as an increase in storage modulus ($G'$) with increasing strain amplitude ($\gamma^\%$). While it is not clear what the exact mechanism behind strain-stiffening is, it is generally ascribed to the rigidity of the network filaments. We want to investigate if micellar gels formed by the VES show strain-stiffening. This line of inquiry is inspired by findings in [68] where it was found that even transient networks of entangled reverse micelles can also show this phenomenon, and by [31] in which surfactant based organogels showed strain stiffening. These organogel’s linear rheology showed frequency independent moduli and their plateau modulus depended on concentration as $-G_p \sim \gamma^{2.1}$, both features similar to that shown by our wormlike micellar gels. It was noted that these organogels also owe their gel-like characteristics to an entangled network of filaments, much like aqueous solutions of F-Actin [31]. Again, this is similar to the generalis of gel-like rheology hypothesized for solutions of EDAB [25] and the VES employed in this study. However, as seen in Fig 11, wormlike micellar gels formed by VES do not display strain-stiffening. We note that beyond the linear regime i.e $\gamma^\% \geq 50$, it becomes extremely difficult to obtain steady alternating states, presumably because of the elasticity of the gels. Data in Fig 11 suggests that VES strain-softens or thins, which is typical for polymeric networks.

In such materials, $G'$ reduces with increasing $\gamma^\%$, because large deformations weaken networks that lend rigidity. Micellar gels are marked by topological interactions and its possible that large strains weaken entanglements, leading to the observed strain-softening response. To understand the strain-stiffening response of transient network of reverse micelles, in [68] the authors proposed that an oscillatory shear of large amplitude can add loose micelles to the network, which can then contribute in increasing stiffness. Such a shear can also remove micelles via disentanglement from the network, an effect that becomes weaker with decreasing flexibility of micelles. A balance of these two opposing effects dictates if entangled micellar networks stiffen or soften under increasing deformation amplitude. It is likely that our wormlike micellar gels do not maintain this balance as is also evident from the lack of shear-thickening in imposed shear-rate tests. Note, shear-thickening was an accompanying response observed in strain-stiffening reverse micelle networks. If this mechanism for strain-stiffening proposed by [68] holds, it should, in principle, be possible to engineer micellar gels with strain-stiffening properties by precisely tuning polydispersity and persistence length.

FIG. 11. Strain controlled amplitude sweep for 8% VES at 2π rad/s frequency at 25°C. Red circles: $G'$, Blue squares: $G''$, Black triangle: $\sigma^*$. In such materials, $G'$ reduces with increasing $\gamma^\%$, because large deformations weaken networks that lend rigidity. Micellar gels are marked by topological interactions and its possible that large strains weaken entanglements, leading to the observed strain-softening response. To understand the strain-stiffening response of transient network of reverse micelles, in [68] the authors proposed that an oscillatory shear of large amplitude can add loose micelles to the network, which can then contribute in increasing stiffness. Such a shear can also remove micelles via disentanglement from the network, an effect that becomes weaker with decreasing flexibility of micelles. A balance of these two opposing effects dictates if entangled micellar networks stiffen or soften under increasing deformation amplitude. It is likely that our wormlike micellar gels do not maintain this balance as is also evident from the lack of shear-thickening in imposed shear-rate tests. Note, shear-thickening was an accompanying response observed in strain-stiffening reverse micelle networks. If this mechanism for strain-stiffening proposed by [68] holds, it should, in principle, be possible to engineer micellar gels with strain-stiffening properties by precisely tuning polydispersity and persistence length. Another detail is the increase in $G''$ with $\gamma^\%$ in the nonlinear regime for the 8% VES. Before we discuss this further, it is imperative to mention that data in the nonlinear regime is not drawn from steady state responses and as such the values of $G''$ at amplitudes in that regime might change if we wait for long enough time to achieve steadiness. However, we expect that the presence of an overshoot should not be affected.
The overshoot in loss modulus is a feature that is observed in many different soft materials (See [69] and references contained therein) and thus the mechanism for it should be structure agnostic [69]. One such mechanism proposed that could apply to our micellar gels, is that as strain amplitude is increased, the nature of strain acquired by the network changes from being recoverable to unrecoverable. Note that the overshoot (usually called Type III) response is different from what is expected from conventional viscoelastic worm-like micellar solutions which show no overshoot (Type I) response. We find that VES revert back to type-I response at a concentrations of 1% as seen in Fig. 12. Thus, the type-III response shown by VES at high concentration is akin to the yielding displayed by soft gels and viscoelastic solids, whereas at lower concentrations VES’s behaviour in strain-amplitude tests is similar to viscoelastic liquids.

D. Shear Rheology

After probing the rheological behaviour of wormlike micellar gels in some detail using oscillation-based tests, we now move on to discussing the shear rheology of these materials. We first report behaviour in shear-startup tests. For this test we follow the same pre-shear+rest protocol outlined in the methods section except that during the rest period, we monitor the evolution of $G', G''$, by imposing oscillations at 1% strain and $\pi$ rad/s frequency. After the end of this protocol (i.e at $t=0$), we impose a constant shear-rate, $\dot{\gamma}$ and record the evolution of the shear-stress signal, $\sigma(t)$. Because we use a stress-controlled rheometer to impose a constant $\gamma$, there is a delay between when the rate imposed by the rheometer, $\gamma_{imp}$ matches the desired shear-rate, $\gamma_{des}$. Thus, we report $\sigma(t)$ from $t = 10s$ onwards, after which $\gamma_{imp}$ is much closer to $\gamma_{des}$. The two solid curves seen in Fig. 13 show a characteristic stress overshoot phenomenon - a growth of stress up to a maximum followed by a decrease of $\sigma$ towards an eventual steady state. Note that in the data presented in Fig. 13, $\sigma$ has not reached steady state and it typically takes a very long time to attain it at such low values of $\dot{\gamma}$. The thin lines in Fig. 13 are stress curves for an elastic response i.e a linear growth $\sigma(t) = G'\dot{\gamma} = G\gamma$. The two dashed lines for each VES concentration differ in the values of $G'$, the lower one extracted from initial time experimental data and the higher one has $G' = G'(t = 0)$ taken from the end of the rest stage. The mismatch between the experimental curve and dashed lines (especially for 8% VES) in Fig. 13 possibly results from residual stresses post the rest stage that is imposed before shear. An interesting feature of the solid curves in Fig. 13 is their deviation from an elastic driven linear growth after $t \gtrsim 500s$ i.e $\gamma \gtrsim 0.5$ or 50% (200s, 20%) if we consider the higher dashed line, after which the value of $\sigma(t)$ is less than that predicted by a purely elastic response.

In an elastic response, strain is accumulated in recoverable fashion. The deviation that preempts eventual "failure" in the material is thus characteristic of the material accumulating strain which is irrecoverable in nature. This harkens back nicely to results discussed in the previous section where we showed that for 8% VES (Fig. 11), there is an overshoot in $G''$ with increasing strain amplitude and noted that a possible reason for this overshoot in the loss modulus is acquisition of irrecoverable strain [69]. Note that in Fig. 11 $G''$ starts increasing with strain amplitude at an approx. $\gamma$% which correlates well with the $\gamma = \dot{\gamma}$ at which the solid red line in Fig. 13 begins to lag behind the elastic response, signalling onset of irrecoverable strain acquisition. The start-up shear response in Fig. 13 is similar to the response of carbolipid microgel reported in [43] where the authors interpreted deviation from an elastic response as the accumulation of plastic strain that eventually leads to an elasto-plastic type failure. This conclusion was backed by velocimetry data. Additionally, there is evidence of their carbolipid microgel undergoing a

![Graph](image-url)
primary creep response marked by \( \dot{\gamma} \sim t^{-\alpha} \) - a power-law scaling called Andrade creep [20] which often indicates plasticity in the system [43][71]. Our wormlike micellar gels also show such a power-law creep scaling under the influence of an imposed shear-stress (See inset of Fig. [14]). We must note that, in general, an irrecoverable strain can be acquired by not only plastic events but also viscous flow within the material network. Indeed, a power-law creep was associated to the latter process in the case of Casein based protein-gels [72]. Details of power-law creep, its possible genesis and related flow will be discussed in a forthcoming publication.

Next, we carry out start-up shear tests at higher shear-rates \( (\dot{\gamma} > 0.01 \text{s}^{-1}) \). From Fig.15 below, we see that the response in this regime is markedly different from that discussed above for very low \( \dot{\gamma} \). Here, a very short-time initial response (low deformation) is elastic and is followed by a micellar network hardening under shear. It is unclear at this point why the effect of such strain-hardening was not captured in tests discussed in the previous section. Under the deformation imposed in this regime, \( \sigma \) keeps increasing up to a peak value, \( \sigma_c \) and then suddenly drops at a value of strain \( \gamma^\% = \gamma_c^\% \) as the network fractures.

At, \( \gamma^\% = \gamma_c^\% \), the rotor bob rapidly accelerates due to the fracture and this is evident in the inset of Fig.15 in which for the specific case shown, \( \gamma_{imp} \) rapidly increases by an order of magnitude around \( \gamma_c^\% \). After this, the rheometer adjusts to the desired shear-rate, \( \dot{\gamma}_{des} = 0.03 \). An interesting aspect ascertained from Fig.15 is that both \( \sigma_c \) and \( \gamma_c^\% \) do not seem to follow any trend with respect to the shear-rate employed to induce deformation. Rather, for one decade in \( \dot{\gamma} \), we see that \( \gamma_c^\% \in (5 - 6.5) \) and \( \sigma_c \in (45 - 65)\text{Pa} \). For experiments carried out with 8\% VES, \( \gamma_c^\% \in (4 - 5) \) and \( \sigma_c \in (100 - 135)\text{Pa} \). We note that this spread in \( \gamma_c^\% \) and \( \sigma_c \) can likely result from inherent stochasticity that may characterise the fracture process. Indeed, we find a spread in times taken by the micellar gel to ‘fluidize’ under a constant shear-stress as well, much like that observed in the fracture process governing polymer gels [73]. Fracture in micellar networks showing slow dynamics has also been shown to have a rate-independent \( \chi \) with some spread (See Fig.13 in [74]). However, that both \( \gamma \) and \( \sigma \) are insensitive to applied rate of deformation certainly merits discussion. To the best of our knowledge, shear-startup studies for system akin to our surfactant gels have not been systematically carried out. The study of fracture in complex fluids has however been an active field of research [75]. One of the models that is routinely employed to model fracture phenomenon in transient networks is the Activated Bond Rupture (ABR) in which the dissociation of bonds in a network is enhanced due to an applied stress. The model was invoked for the case of polymer gels in [73] and it predicts the critical strain for fracture \( \gamma_c \sim C_1 \ln(C_2 \dot{\gamma}) \) and thus \( \sigma_c \sim C_1 \ln(C_2 \dot{\gamma}) \) \( (C_1, C_2 \text{ are material dependent constants}) \). i.e - the rupture strain and stress have a logarithmic dependence on applied rate of deformation. As mentioned before however, no such dependence is found in our experiments. A shear-rate independent rupture strain was found in a lecithin-cyclohexane system that forms a wormlike micellar network [74], but the shear-stress at rupture strongly depends on \( \dot{\gamma} \) in the fracture regime. The authors proposed that the fracture in this system is characterized by a uniformly accelerating fracture driven by breakage of micellar strands. Their post-fracture state consists of a nematic phase populated by disentangled and highly aligned micelles.

This fracture mechanism does not apply to our system for two reasons - (1): it is unlikely that micellar breakage plays a role in the fracture as it was argued that for order unity deformations, micellar chains between entanglements store an elastic energy \( \sim O(k_B T/L_c) \) [76] which for \( L_c \sim O(10^3) \text{nm} \) is much smaller than the scission energies (even if the effective scission energy is reduced by an applied force). In any case
Rheology of Wormlike Micellar Gels

the achieved $\sigma$ in our rheology experiments seem to be much smaller than micellar breaking stresses reported in previous studies [77, 78] (2): Our results clearly show that after the stress rapidly drops, the sheared material has a distinct elastic behavior. More studies [77, 78] (2): Our results clearly show that after the stress rapidly drops, the sheared material has a distinct elastic behavior. Same as main figure but for 4.5% VES. Inset: The average value of the exponent extracted from the data in Fig. [17] is $\alpha \approx 0.72$. To obtain a proper estimate of $\alpha$ would require conducting multiple flow-curve experiments and averaging over independent runs at each $\dot{\gamma}$, so our estimate of $\alpha$ should at best be looked as a rough estimate. But, we note that this scaling lies somewhere in between $\alpha = 0.77$ and 0.66, which are predictions made for flexible micelles and more rigid micelles respectively [80]. A scaling of $\alpha \approx 0.66$ was also reported for the flow of EHAC [87]. The average value of the exponent extracted from the data in [17] is $\alpha \approx 0.72$. To obtain a proper estimate of $\alpha$ would require conducting multiple flow-curve experiments and averaging over independent runs at each $\dot{\gamma}$, so our estimate of $\alpha$ should at best be looked as a rough estimate. But, we note that this scaling lies somewhere in between $\alpha = 0.77$ and 0.66, which are predictions made for flexible micelles and more rigid micelles respectively [80]. A scaling of $\alpha \approx 0.66$ was also reported for the flow of EHAC [87].

For flow-curves, we sweep downwards from $\dot{\gamma} = 10^3 \text{s}^{-1}$ to $10^{-3} \text{s}^{-1}$ by adjusting the waiting time at each $\dot{\gamma}$. We report results up to $\dot{\gamma} = 10^{-3} \text{s}^{-1}$ because at lower rates, $\sigma$ takes very long time to reach steady-state. For $\dot{\gamma} > 1 \text{s}^{-1}$, VES show a marked shear-thinning behaviour, $\eta \sim \dot{\gamma}^{-\alpha}$ or $\sigma \sim \dot{\gamma}^{-\alpha}$. The average value of the exponent extracted from the data in the shear-thinning regime. As seen in the bottom inset of Fig. [17] when $\dot{\gamma}$ is stepped down, there is a rapid drop in stress, followed by a build-up to the steady-state stress at $\dot{\gamma} = 10^{-1} \text{s}^{-1}$. This rapid drop indicates that for $\dot{\gamma}$ in this regime, the shear-thinning behaviour arises due to aligned micelles that form a viscous nematic phase which allows stress to relax almost instantaneously when $\dot{\gamma}$ is dropped. The stress build-up post drop-off indicates re-building of stress-bearing microstructure. Taken together, this behaviour is suggestive of a thixotropic response in this regime [88, 90]. We also note that for $\dot{\gamma}$ between $0.05 - 1 \text{s}^{-1}$, the value of $\alpha$ is markedly smaller than that in the shear-thinning regime. This range of $\dot{\gamma}$ coincides with the range in which we have characterised a fracture behaviour earlier and the transition in the value of $\alpha$ can indicate a structural change in the micelles, the physical mechanism for which remains elusive at this point.

Another interesting features of the flow-curves in Fig. [17] is their non-monotonicity wherein for $\gamma \lesssim 0.01 \text{s}^{-1}$, $\sigma$ increases with decreasing $\dot{\gamma}$. A caveat is necessary before we proceed with discussing this feature. At these low values of $\dot{\gamma}$, the time taken to reach steady-state becomes very large and this makes steady-state flow-curve experiments difficult. Thus, the points ($\dot{\gamma} \lesssim 0.01 \text{s}^{-1}$) in the flow-curve likely represent a transient scenario, rather than a true steady state. However, we can still gain some valuable insight from these experiments.

In principle, an intrinsic non-monotonic flow-curve is often a signature of shear-banding in the system, but the experimental manifestation of this phenomenon is a stress-plateau.

in our data. Clearly, there is much to uncover about the failure scenario in this regime. Preliminary experiments suggest that the presence of a fracture can be altered by the nature of rest before imposing a shear-rate. Indeed, such fracture dynamics have been shown to be dependent on boundary conditions and material history [83, 84]. Disentangling the role of these in the phenomenon displayed by our micellar gels is out of scope of the present paper. In order to better understand this interesting fracture regime and rule out other possible mechanisms like wall-slip, further detailed studies are required, starting with characterizing the dynamics of these wormlike micellar gels under an imposed shear stress. Such a study is currently under way [85]. We end this section on shear-rheology with a discussion on ‘flow-curves’ exhibited by VES solutions.

For flow-curves, we sweep downwards from $\dot{\gamma} = 10^3 \text{s}^{-1}$ to $10^{-3} \text{s}^{-1}$ by adjusting the waiting time at each $\dot{\gamma}$. We report results up to $\dot{\gamma} = 10^{-3} \text{s}^{-1}$ because at lower rates, $\sigma$ takes very long time to reach steady-state. For $\dot{\gamma} > 1 \text{s}^{-1}$, VES show a marked shear-thinning behaviour, $\eta \sim \dot{\gamma}^{-\alpha}$ or $\sigma \sim \dot{\gamma}^{-\alpha}$. The average value of the exponent extracted from the data in Fig. [17] is $\alpha \approx 0.72$. To obtain a proper estimate of $\alpha$ would require conducting multiple flow-curve experiments and averaging over independent runs at each $\dot{\gamma}$, so our estimate of $\alpha$ should at best be looked as a rough estimate. But, we note that this scaling lies somewhere in between $\alpha = 0.77$ and 0.66, which are predictions made for flexible micelles and more rigid micelles respectively [80]. A scaling of $\alpha \approx 0.66$ was also reported for the flow of EHAC [87].

A typical step-down in shear experiment ($\dot{\gamma} = 10^3 - 10^{-1} \text{s}^{-1}$) offers some insight into the state of VES when deformed by a $\dot{\gamma}$ in the shear-thinning regime. As seen in the bottom inset of Fig. [17] when $\dot{\gamma}$ is stepped down, there is a rapid drop in stress, followed by a build-up to the steady-state stress at $\dot{\gamma} = 10^{-1} \text{s}^{-1}$. This rapid drop indicates that for $\dot{\gamma}$ in this regime, the shear-thinning behaviour arises due to aligned micelles that form a viscous nematic phase which allows stress to relax almost instantaneously when $\dot{\gamma}$ is dropped. The stress build-up post drop-off indicates re-building of stress-bearing microstructure. Taken together, this behaviour is suggestive of a thixotropic response in this regime [88, 90]. We also note that for $\dot{\gamma}$ between $0.05 - 1 \text{s}^{-1}$, the value of $\alpha$ is markedly smaller than that in the shear-thinning regime. This range of $\dot{\gamma}$ coincides with the range in which we have characterised a fracture behaviour earlier and the transition in the value of $\alpha$ can indicate a structural change in the micelles, the physical mechanism for which remains elusive at this point.

Another interesting features of the flow-curves in Fig. [17] is their non-monotonicity wherein for $\gamma \lesssim 0.01 \text{s}^{-1}$, $\sigma$ increases with decreasing $\dot{\gamma}$. A caveat is necessary before we proceed with discussing this feature. At these low values of $\dot{\gamma}$, the time taken to reach steady-state becomes very large and this makes steady-state flow-curve experiments difficult. Thus, the points ($\dot{\gamma} \lesssim 0.01 \text{s}^{-1}$) in the flow-curve likely represent a transient scenario, rather than a true steady state. However, we can still gain some valuable insight from these experiments.

In principle, an intrinsic non-monotonic flow-curve is often a signature of shear-banding in the system, but the experimental manifestation of this phenomenon is a stress-plateau.
The region of the flow-curve where non-monotonicity occurs is experimentally inaccessible because for shear-rates in this regime, the material separates into two or more shear-bands. However, a measurable non-monotonicity in the flow-curve can be closely related to transient shear-banding. In the authors showed that a competition in breakup and restoration (ageing) of stress-bearing microstructure can lead to regions where measured $\sigma$ increases with decreasing imposed $\dot{\gamma}$ and this directly correlates with banding observed in their Laponite system. Indeed, as suggested in direct analogies can be drawn between their colloidal gel system and our wormlike micellar gel, where disentanglement/re-entanglement can play the role breakup/ageing and the stress-bearing microstructure is essentially a network of long entangled micelles. Prominent stress-overshoot at very low $\dot{\gamma}$ along with the very long times to reach steady in this regime, both generally features of shear-banding often observed in wormlike micellar solutions, are also observed in our surfactant gels. This supports the occurrence of shear-banding in our system. Note, that disentanglement of micellar strands is at the heart of a proposed mechanism for shear-banding in WLM solutions, wherein progressive disentanglement leads to gradual development of shear-bands. The cup-bob geometry aids this mechanism due to its inherent stress gradient and has been reported to aid the formation of shear-bands in systems with flow-curves that are nearly non-monotonic, further lending credence to the presence of shear-banding in our system. The above invoked mechanism is likely distinct from the one suggested for causing fracture for higher values of $\dot{\gamma}$. It is possible that fractures do not form in the low $\dot{\gamma}$ regime because re-entanglement can ‘heal’ zones of depleted entanglements. It is imperative to mention here that the ‘measured’ non-monotonicity in the flow-curves for the VES are distinct from the flow-curves in granular media, microemulsions of oil-water and waxy crude oils, where the resulting measurable non-monotonicity is usually indicative of an unstable flow. While we cannot confirm the nature of shear-bands with certainty in this paper owing to absence of local data and long timescales involved, it is likely that the ‘transient’ bands that cause non-monotonicity in our flow curves, persist over long-times into a permanent band at steady state, finally manifesting rheologically as a stress-plateau. Finally, we end this section by noting that there is precedent for non-monotonic flow-curves in a surfactant gel-system formed by long-chained zwitterionic surfactants.

In authors employed EDAS - a zwitterionic amidosulfobetaine surfactant gel, and demonstrated that flow-curve experiments with this system showed non-monotonicity. The authors tied this to the presence of shear-banding, by visually confirming bands (although no comment was made on if these bands are transient or steady). There are some crucial differences between results reported in and our paper.

First, they were able to experimentally access the ‘Newtonian’ regime of the system in which $\sigma \propto \dot{\gamma}$ and no-overshoot appears in shear-startup tests. This guarantees that the surfactant ‘gel’ isn’t a true bulk gel and its yielding characteristics are crucially tied to the shear-banding transition and the peak stress extracted from the non-monotonic region of the flow-curve. We observe an overshoot for the lowest shear-rate tested $\dot{\gamma} = 10^{-3}(s^{-1})$ (As seen in Fig. 14) and owing to long experimental times, could not access the Newtonian regime. However, as seen in Fig. 18 for the controlled-stress run, we are close to probing the Newtonian regime. The inset in Fig. 18 confirms that steady state is reached for the lowest $\sigma$ values (Although we are close to the operating limit of the rheometer with such low values of $\sigma, \dot{\gamma}$). This suggests that our micellar gels too are not bulk gels. It is likely that the apparent yield-stress in our system too can be tied to a banding transition and gel-like rheological behaviour can be...
CONCLUSION

In this paper we conducted a detailed linear and non-linear rheological study of surfactant gel formed by long-chained zwitterionic surfactants. We showed that this system has a microstructure made up of long entangled wormlike micelles and demonstrated gel-like behaviour in its linear-rheology at 25°C and on visual inspection, much like that displayed by similar systems \[20\]–\[22\]. Our analysis of the viscoelastic state at 60°C and higher temperatures allowed us to calculate time-scales associated with the system’s rheological response as well as various activation energies that govern these quantities. We showed that these timescales do not obey scalings derived for more conventional surfactant systems. Our results call for further theoretical and experimental studies to resolve measured deviations from current theory for wormlike micellar systems and to gain better understanding of the self-assembly of long-chained surfactants. We also showed the absence of strain-stiffening in these surfactant gels, a behaviour contrary to that exhibited by similar systems \[31\]–\[38\] but in agreement with a system closest to ours - EDAB \[104\]. Our shear rheology results revealed an interesting fracture regime reminiscent of brittle type fracture seen in amorphous materials \[105\]–\[106\], the specifics of which have not been earlier reported for a micellar system to the best of our knowledge. We compared this behaviour to similar dynamics reported for other systems and outlined a possible mechanism for the same. A similar shear-induced fracture has been reported for certain telechelic protein based hydrogels \[107\]. Here, the related shear-banding behaviour is beneficial as it shields cells embedded in tissue matrices made from these hydrogels from damage during injection. As surfactant gels are being seen as alternatives to polymer based hydrogels for biomedical applications \[28\], insight into shear-induced failure in such materials will inform design of smart and efficient soft matter.

While, in the fracture regime, it is likely that the velocity field is inhomogeneous (in addition to/because of shear-banding), our flow-curves provide indirect evidence of transient shear-banding in our wormlike micellar gels. Extremely slow transients mark the stress response in this regime and it is difficult to measure a steady-state response; instead we see a non-monotonic flow-curve. If indeed, micellar disentanglement drives eventual response in both the fracture and possible transient-banding regime, this surfactant gel is then an appropriate system to study two different mechanisms of strain localization \[80\]. Finally, we show that it is likely that surfactant gels are not true ‘gels’ but essentially ‘fluids’ with ultra-long relaxation times (If we go by Fig.18 relaxation time \(\sim O(10^2)\)s) and this can explain the long transients in the flow-curve’s non-monotonic region. This finding makes an advance in answering the conundrum of gelation induced only by entanglements \[25\] and suggests that while a surfactant gel might show many gel-like features in its appearance and rheology, and even if it may sometimes functionally behave like a gel owing to its very high relaxation time, it is not a permanent gel \[103\]. Overall, this paper establishes wormlike micellar gels formed by long-chained zwitterionic surfactants as a fertile model system to explore a gamut of phenomena prevalent across soft matter. In the future, we plan to better elucidate the failure/fracture mechanisms of these gels - in particular the possible roles of disentanglement in the bulk and wall-slip in this driving this phenomenon. We also plan to check if our wormlike micellar gels display novel behaviour in extensional flow and other canonical flow scenarios. The results presented in this paper are likely to inform these studies and other such studies that deal with the formulation, characterization and flow dynamics of similar systems.

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