Wormlike Micelles of a C22-Tailed Zwitterionic Betaine Surfactant: From Viscoelastic Solutions to Elastic Gels

Rakesh Kumar,‡ Gokul C. Kalur,†,§ Lior Ziserman,∥ Dganit Danino,∥ and Srinivasa R. Raghavan*†

Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland 20742-2111, and Department of Biotechnology and Food Engineering, Technion—Israel Institute of Technology, Technion, Haifa, Israel 32000

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The 22-carbon-tailed zwitterionic surfactant erucyl dimethyl amidopropyl betaine (EDAB) forms highly viscoelastic fluids in water at low concentrations and without the need for salt or other additives. Here, semidilute aqueous solutions of EDAB are studied by using a combination of rheological techniques, small-angle neutron scattering (SANS) and cryo-transmission electron microscopy (cryo-TEM). EDAB samples show interesting rheology as a function of temperature. At low temperatures (~25 °C), a 50 mM EDAB sample behaves like an elastic gel with an infinite relaxation time and viscosity. Upon heating to ~60 °C, however, the sample begins to respond like a viscoelastic solution; that is, the relaxation time and zero-shear viscosity become finite, and the rheology approaches that of a Maxwell fluid. The same pattern of behavior is repeated at higher EDAB concentrations. Cryo-TEM and SANS reveal the presence of giant wormlike micelles in all EDAB samples at room temperature. The results imply that, depending on temperature, EDAB wormlike micelles can exhibit either a gel-like response or the classical viscoelastic (“Maxwellian”) response. The unusual gel-like behavior of EDAB micelles at low temperatures is postulated to be the result of very long micellar breaking times, which, in turn, may be due to the long hydrophilic tails of the surfactant.

1. Introduction

It is well-known that surfactant molecules can assemble in aqueous solution to form long, flexible, cylindrical chains with contour lengths of a few micrometers.1–4 These “wormlike” or “threadlike” micelles typically become entangled into a transient network, thereby imparting viscoelastic properties to the solution. Initial work on these structures (about 20 years ago) focused on their similarities and differences with conventional polymers in solution.1 While polymers are held by strong, covalent bonds that are not easily broken, wormlike micelles are held by weak, physical bonds that continuously break and re-form. There is thus a continuous exchange of surfactant unimers between micelles, and the micellar breaking dynamics influences the rheological properties of the fluid. Also, because the micelles are essentially in thermal equilibrium with their unimers, the average micellar length $L$ behaves as a thermodynamic quantity and changes with solution composition and temperature.1

From a rheological standpoint, wormlike micelles typically exhibit a viscoelastic response with a finite relaxation time.1–4 This relaxation time equals the geometric mean of the micellar breaking time $\tau_b$ and the chain reptation time $\tau_{rep}$ in the limit of fast-breaking micelles ($\tau_b \ll \tau_{rep}$).5 In this limit, the rheological response becomes close to that of a Maxwell fluid (i.e., an idealized viscoelastic fluid with a single relaxation time) and the stress relaxation function corresponding becomes a monoexponential decay. If instead $\tau_b$ is comparable in magnitude to $\tau_{rep}$, the rheological response shows a spectrum of relaxation times.1,2 The dominant relaxation time in such cases is often estimated from the dynamic frequency spectrum as the inverse of the crossover frequency $\omega_c$, at which the elastic modulus $G'(\omega)$ and the viscous modulus $G''(\omega)$ cross.6 It is worth emphasizing that, in all the above cases, the relaxation time is finite; in other words, at long time scales (low frequencies), the fluid always relaxes and the moduli $G'(\omega)$ and $G''(\omega)$ fall to zero.

In this paper, we report the rheology of zwitterionic wormlike micelles formed by a C22-tailed betaine surfactant. We show that the rheology of these fluids is qualitatively different from the cases discussed above. Specifically, at low temperatures, the fluids are true “permanent” gels, with the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, remaining finite (nonzero) at low frequencies and the elastic modulus $G'(\omega)$ exceeding the viscous modulus $G''(\omega)$ over the entire range of frequencies. This rheology is reminiscent of a cross-linked polymer gel rather than an entangled network of wormlike chains.3 When the same fluids are heated above ~60 °C, however, the rheology reverts to the viscoelastic (Maxwellian) response commonly associated with wormlike micelles. To conclusively establish the microstructure in these fluids, we use cryo-transmission electron microscopy (cryo-TEM) and small-angle neutron scattering (SANS). Both of these techniques confirm that the samples do contain long wormlike micellar chains over the entire range of temperatures. Thus, the key result from the present study is that wormlike micelles can behave either as elastic gels or as viscoelastic solutions, depending on their composition and temperature. It is important to point out that, although earlier studies have often referred to wormlike micellar fluids as gels or gel-like,4,6 these systems invariably do not satisfy the strict rheological definition of a permanent gel (i.e., they do not exhibit a nonzero equilibrium modulus).

* To whom correspondence should be addressed. E-mail: sraghava@eng.umd.edu.
† University of Maryland.
‡ Technion—Israel Institute of Technology.
§ Present address: Irix Pharmaceuticals, Inc., Florence, South Carolina.
Scheme 1. Chemical Structures of the Surfactant and Salts Used

Our interest in the system studied in this paper arose due to two reasons. First, the rheological properties of these fluids render them useful for various applications. As mentioned, the fluids are gels at low temperatures and they also retain a very high viscosity and viscoelasticity at high temperatures (＞80°C). Erucyl dimethyl amidopropyl betaine (EDAB) could thus be useful as a thickening agent for water in a variety of consumer formulations. A second aspect of interest is that the surfactant involved is zwitterionic. The majority of wormlike micellar systems studied in the past have been based on cationic surfactants. There are only a few studies on worms formed by zwitterionic surfactants, many of which have focused solely on alkyl dimethylamine oxides. Despite the relative lack of interest from academia, zwitterionic surfactants are very popular commercially, since they tend to be very gentle on human skin and on the environment. Thus, an improved understanding of zwitterionic worms is likely to have both fundamental and commercial significance.

2. Experimental Section

Materials. The EDAB surfactant was a commercial product manufactured by Rhodia Inc., Cranbury, NJ. EDAB is a zwitterionic surfactant of the betaine type, as shown by its chemical structure. Manufactured by Rhodia Inc., Cranbury, NJ. EDAB is a zwitterionic surfactant for water in a variety of consumer formulations. Dimethyl amidopropyl betaine (EDAB) could thus be useful as a thickening agent for water in a variety of consumer formulations. The EDAB surfactant was a commercial product (Scheme 1), with the molecule having both a positively charged dimethylammonium moiety and a negatively charged carboxylate group. The as-supplied commercial product contained sodium dimethylammonium moiety and a negatively charged carboxylate (NaHNC). The as-supplied commercial product contained sodium hydroxynaphthalene carboxylate (NaHNC). The as-supplied commercial product contained sodium hydroxynaphthalene carboxylate (NaHNC), with the molecule having both a positively charged dimethylammonium moiety and a negatively charged carboxylate group.


3. Results

EDAB Solutions: Phase Behavior and Rheology. We begin by discussing the phase behavior and rheology of EDAB solutions as a function of EDAB concentration and temperature. Because EDAB is a zwitterionic surfactant, electrostatic repulsions between its headgroups will be weak. Moreover, EDAB also has a very long erucyl (C22) tail, and these two factors together suggest that the critical micelle concentration (CMC) of EDAB in water will be extremely low (＜1 μM). In addition, the cis-unsaturation and resulting kink in the erucyl tail (Scheme 1) help to ensure that EDAB also has a low Krafft point. Thus, EDAB solutions are stable for months at room temperature and they do not from crystalline precipitates when cooled.

The low CMC also ensures that EDAB micelles will start to grow at very low concentrations, in turn impacting the solution rheology. Figure 1 shows photographs of selected EDAB samples, and Figure 2 presents rheological data for these samples at 25°C. At 0.8 mM EDAB, the viscosity of the solution is slightly higher than that of water (Figure 2a). The viscosity increases by 1 order of magnitude when the concentration is increased to 2.5 mM EDAB. A further increase in EDAB concentration to 8 mM imparts a weak yield stress to the sample, and the yield stress increases with further addition of EDAB. Photographs of the 25 and 50 mM EDAB samples (Figure 1) reveal their yield stress (gel-like) behavior. In both of these samples, bubbles are observed to be trapped due to the gel-like nature of the material. The yield stress of the 50 mM gel is also sufficiently high such that it can

stored at room temperature for at least 1 day before running experiments. For SANS experiments, samples were made in D2O (99.5%, from Cambridge Isotopes).

Rheology. Steady and dynamic rheological experiments were performed on an AR2000 stress controlled rheometer (TA Instruments, Newkirk, DE). Samples were run on a cone-and-plate geometry (40 mm diameter, 2° cone angle) or a couette geometry (rotor of radius 14 mm and height 42 mm, and cup of radius 15 mm). The temperature was controlled to ±0.1°C of the desired value. Samples were equilibrated at the temperature of interest for at least 20 min prior to experimentation. A solvent trap was used to minimize water evaporation. Dynamic frequency spectra were conducted in the linear viscoelastic regime of the samples, as determined from dynamic stress sweep measurements.

Small-Angle Neutron Scattering (SANS). SANS measurements were made on the NG-3 (30 m) beamline at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD. Samples were studied in 2 mm quartz cells. The scattering spectra were corrected and placed on an absolute scale using calibration standards provided by NIST. The data are shown for the radially averaged, absolute intensity I versus the scattering vector q = 4π sin(θ/2)/λ, where λ is the wavelength of incident neutrons and θ is the scattering angle.

Cryo-TEM. The cryo-TEM work was done at the Hanna and Georg Krumholz Laboratory for Advanced Microscopy at Technion-IIT. Samples for cryo-TEM were prepared in a controlled environment vitrification system (CEVS). In this apparatus, samples at the desired temperature are quenched rapidly into liquid ethane at its freezing point of -183°C, forming a vitrified specimen, and then transferred to liquid nitrogen for storage. The vitrified samples were examined on a Philips CM120 microscope operated at 120 kV, using an Oxford CT-3500 cryo-holder for keeping the samples below -180°C. Digital images were recorded in the minimal electron dose mode by a Gatan 791 Multiscan cooled charge-coupled device (CCD) camera.
support its own weight in an inverted or tilted vial. Figure 1 also shows that the 25 and 50 mM EDAB samples are flow-birefringent; that is, they exhibit bright streaks (visible under crossed polarizers) when the vial is shaken or tilted.

It is evident from Figure 1 that small amounts of EDAB impart high viscosities to aqueous solutions. Such high viscosities as well as the flow-birefringence are typical features of samples containing wormlike micelles.\(^1\)-\(^4\) What is unusual, however, is the presence of a true yield stress, that is, an elastic gel-like response, in many EDAB samples. This aspect is further explored through dynamic rheological measurements, as shown in Figure 2a. Here, the elastic modulus \(G^\prime\) and viscous modulus \(G^\prime\prime\) are plotted as functions of frequency \(\omega\) for various EDAB samples. Only the sample with the lowest EDAB content of 0.8 mM shows a viscous response, with \(G^\prime\) exceeding \(G^\prime\prime\) over the entire frequency range and with both moduli being strong functions of frequency. All the other samples (2.5 mM EDAB or higher) show a very different dynamic rheological response, with \(G^\prime\) exceeding \(G^\prime\prime\) and both moduli being independent of frequency. The frequency-independence implies that there is no relaxation of stress even at long time scales; that is, these EDAB samples respond like elastic gels with infinite relaxation times.\(^5\)

The gel-like character of EDAB samples is also reflected in steady-shear rheology as an apparent yield stress for these samples. Figure 2b shows the apparent viscosity of the above EDAB samples as a function of the shear stress. The yield stress behavior is especially apparent for the 8 mM and 25 mM EDAB samples. For example, in the case of 8 mM EDAB, the viscosity is essentially infinite at shear stresses below about 2 Pa (which is, thereby, the value of the yield stress for this sample). Above this shear stress, the viscosity rapidly decreases by several orders of magnitude, that is, the sample “yields”.\(^5\) Note that there is no plateau in the viscosity at low stresses, in contrast to the behavior observed typically for a viscoelastic wormlike micellar sample.\(^1\)-\(^4\)

Figure 2 thus shows that the dynamic rheology of EDAB solutions resembles that of a cross-linked polymer gel rather than an entangled network of wormlike chains. In other words, these samples respond in an elastic rather than viscoelastic fashion. We will now show that the same gel-like EDAB samples revert to a viscoelastic response at higher temperatures. Dynamic rheological data at various temperatures are shown for a 50 mM EDAB sample in Figure 3 and for a 100 mM EDAB sample in Figure 4. Both samples exhibit a gel-like response at low temperatures (Figures 3a and 4a). Interestingly, there is a slight increase in \(G^\prime\) and a decrease in \(G^\prime\prime\) from 25 to 40 °C in both cases. At higher temperatures (around 60 °C), the response of both samples switches from gel-like to viscoelastic; that is, at frequencies below a critical value \(\omega_c\), the elastic modulus \(G^\prime\) crosses over and drops below the viscous modulus \(G^\prime\prime\) (Figures 3b and 4b). In other words, the relaxation time \(\tau_R \sim 1/\omega_c\) is finite at high temperatures. The sample response at high temperatures can thus be divided into two regimes based on the relaxation time \(\tau_R\) at time scales much shorter than \(\tau_R\) (i.e., for \(\omega \gg \omega_c\)) the response is elastic, whereas for time scales much longer than \(\tau_R\) (i.e., for \(\omega \ll \omega_c\)) the response is viscous.

The time-dependent viscoelastic response depicted in Figures 3b and 4b is what one usually expects to find for wormlike micelles. It is also known that wormlike micellar systems often behave as Maxwell fluids, that is, with a single dominant relaxation
The Maxwell model gives the following predictions for $G'$ and $G''$ versus frequency:

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

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

Here, $G_p$ is the plateau modulus, that is, the value of $G'$ at high frequencies. Fits to eqs 1 and 2 are shown as solid lines through the data in Figure 3b at 60 and 70 °C. Clearly, the Maxwell model fits the data well at low and intermediate frequencies, confirming that a single relaxation time dominates the rheological response. The discrepancy in $G''$ at high frequencies is known to occur for wormlike micelles: it arises because the micelles are dynamic entities that break and recombine rapidly.

The above data thus confirm that EDAB samples at high temperatures exhibit the classic viscoelastic signature associated with wormlike micelles. The fact that they have a finite relaxation time implies, in turn, that under steady-shear rheology the samples have a finite zero-shear viscosity, not a yield stress. As the temperature is raised, both the relaxation time and the zero-shear viscosity decrease exponentially. This explains why the frequency spectra in Figures 3b and 4b shift in the direction of higher frequencies or shorter time scales with increasing temperature. The exponential drop in $\tau_R$ and $\eta_0$ is mediated by the same parameter, that is, the flow activation energy $E_a$, the value of which can be obtained from an Arrhenius plot of these quantities.

For the 50 mM EDAB sample, the value of $E_a$ from the Arrhenius plot (not shown) is $\sim 181$ kJ/mol, which is comparable to that reported in other studies. It is also worth noting from the rheological data at high temperatures that the plateau modulus $G_p$ is almost constant, that is, independent of temperature.

EDAB Solutions: Structure from SANS and Cryo-TEM.

We have seen that EDAB solutions exhibit many features of wormlike micelles, although the unusual gel-like response at...
low temperatures remains to be explained. It is therefore useful to apply complementary techniques to probe the microstructure in these samples. We have used two such techniques, SANS and cryo-TEM. SANS spectra at 25 °C are shown in Figure 6 for 50, 100, and 150 mM EDAB solutions in D$_2$O (these samples were rheologically identical to those in H$_2$O). All three EDAB solutions asymptote to a slope of −1 on the log-log plot, which is indicative of the $I \sim q^{-1}$ scaling expected for long cylindrical chains.21 As such, the SANS data support the presence of wormlike micelles in the samples even at low temperatures. The increase in scattered intensity with EDAB concentration is simply a reflection of the increasing number density of scatterers.21 The radius of the worms can be obtained using a cross-sectional Guinier plot of the high-$q$ data, that is, a plot of ln($I_q$) versus $q^2$, from which we find a value of ~29 Å for EDAB worms, independent of the concentration (data not shown). This value is quite comparable to the length of a fully extended 22-carbon alkyl tail.17

We have also performed SANS on the 50 mM EDAB sample as a function of temperature. The $I$ versus $q$ plots for this sample at 25, 60, and 80 °C were found to be practically identical (data not shown). This might be considered surprising, since the sample viscosity decreases appreciably over this temperature range (Figure 3b), implying that there must be large decreases in micelle length.1,20 However, SANS only probes relatively short length scales, and it is likely that the micelles are comparatively very long (contour lengths > 10 μm) over the entire temperature range. The data in SANS (corresponding to segments of the micellar chains) will then indeed appear to be invariant with temperature.22,23 Similar results have been reported for other wormlike micellar fluids.22,23

In addition to SANS, we have also used cryo-TEM to study the microstructure in EDAB solutions. Note that cryo-TEM is a technique where the structure in a fluid sample is preserved by rapid freezing under a controlled environment.18,19 Figure 7 shows cryo-TEM images of a 50 mM EDAB sample at room temperature, and we observe very long, entangled wormlike micelles, some as long as 1 μm in contour length. Some of the micelles are stretched out due to the shear applied during cryo-TEM sample preparation.18 Cryo-TEM thus confirms that wormlike micelles are present in EDAB samples at room temperature, in accordance with the SANS data. We also do not observe any other type of structures in the cryo-TEM images that could explain why these samples show a gel-like rheology at low temperatures.

**EDAB Solutions: Effect of Inorganic and Aromatic Salts.** We mentioned in the Experimental Section that the as-supplied EDAB sample contains an equimolar amount of NaCl salt. To examine if this residual salt has an influence on the rheology, we removed the salt by solvent extraction. However, the removal of residual salt had no effect on solution rheology: identical frequency spectra were obtained over the entire range of temperatures for an equivalent concentration of EDAB, regardless of the NaCl concentration. This result is perhaps not surprising, since the main effect of salt is usually to screen the electrostatic interactions between surfactant headgroups. Here, because EDAB is zwitterionic, its headgroups will only have weak electrostatic interactions, and salt will therefore have a negligible effect.14,15 Indeed, this insensitivity to added salt is one of the important advantages of zwitterionic surfactant formulations compared to ionic ones.7,13

While EDAB is insensitive to all common inorganic salts that we have tested, we have observed an interesting sensitivity to certain aromatic salts. Specifically, we have found that the naphthalene salt NaHNC (Scheme 1) reduces the viscosity of EDAB solutions when added at low concentrations. Figure 8 presents steady-shear rheological data at 25 °C for 50 mM EDAB solutions at different NaHNC concentrations. The control EDAB sample is a gel at 25 °C and therefore does not have a viscosity plateau at low shear rates (i.e., its zero-shear viscosity $\eta_0$ is

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Figure 6. SANS scattering spectra at 25 °C for 50, 100, and 150 mM EDAB solutions in D$_2$O. The data asymptote to a slope of −1 at low values of the wave vector $q$.

Figure 7. Cryo-TEM images of the microstructure in a 50 mM EDAB sample at room temperature.
Figure 8. Steady shear rheology of EDAB/NaHNC samples at room temperature (25 °C). The EDAB concentration is 50 mM in all cases, and the NaHNC concentration in each sample is indicated on the plot.

Figure 9. Comparison of the zero shear viscosity $\eta_0$ of EDAB solutions in the presence of two different organic salts, NaHNC and NaSal. The EDAB concentration is 50 mM.

infinite). Adding 30 mM NaHNC converts this elastic gel into a viscoelastic fluid with a high, but finite, $\eta_0$ around 300 Pa.s. Further addition of NaHNC brings the viscosity down further, and finally, for 100 mM NaHNC, the sample is a Newtonian fluid with a viscosity close to that of water. Presumably, the addition of NaHNC reduces the size of EDAB wormlike micelles until the micelles become so short that they cannot entangle. Such a microstructural interpretation is supported by SANS (data not shown), where the $I$ versus $q$ data for a 50 mM EDAB + 100 mM NaHNC sample shows a plateau in the intensity at low $q$, indicating that the wormlike micelles have been transformed into small spheres or ellipsoids.17,21

Why are EDAB micelles sensitive to NaHNC? A related question would be whether such sensitivity is observed with other aromatic salts, and in this context we have compared NaHNC with NaSal (Scheme 1). Our results show that NaSal also has a similar effect as NaHNC but at much higher concentrations. Figure 9 is a comparison of zero-shear viscosity values of 50 mM EDAB solutions in the presence of either NaSal or NaHNC. We find that about 500 mM NaSal must be added to convert a 50 mM EDAB solution to a Newtonian, waterlike fluid, whereas 100 mM NaHNC is sufficient for the same purpose. Note also that about 200 mM NaSal must be added before we begin to see any measurable effect on the rheology. In comparing the molecules, NaSal is identical to NaHNC, except that the former has only one benzene ring. This in turn means that NaSal is less hydrophobic than NaHNC,17 and we will return to this point in the next section in trying to explain our results. To summarize the effects of salts on EDAB solutions, inorganic salts have no effect, while aromatic salts (hydrotopes) may have a weak or strong effect depending on their hydrophobicity.

4. Discussion

We have seen that the zwitterionic surfactant EDAB forms very long wormlike micelles in water. The presence of such worms over the entire temperature range in EDAB samples has been confirmed through a variety of experimental techniques, including SANS and cryo-TEM. However, while these micellar fluids showed the expected viscoelastic response at high temperatures, they behaved as elastic gels at low temperatures. Such gel-like behavior is definitely unusual, and we will attempt to explain it in this section. In this context, there are two aspects regarding the structure of EDAB that are important: (a) it is zwitterionic and (b) it has a very long (C22) tail. With these aspects in mind, it is useful to compare our results for EDAB with those reported in the literature for worms formed by other zwitterionic surfactants8–12 as well as for worms of other C22-tailed ionic surfactants.17,20,22

Comparison with Other Zwitterionic Worms. First, with regard to zwitterionic surfactants, the proximity of their positive and negative charges implies that the net charge on the surfactant headgroup will be quite low (i.e., headgroup repulsions will be weak). As a result, the effective headgroup area will be small, allowing the surfactant molecules to directly form cylindrical micelles. This is in contrast to ionic surfactants, where salt must be added to induce the formation of cylindrical micelles. Direct formation of wormlike micelles in deionized water in the absence of salt has been observed previously for zwitterionic surfactants.8–12 For example, C16- and C18-tailed carboxybetaines form such micelles at concentrations greater than ~50 mM, whereas C12- and C14-tailed carboxybetaines only form spherical micelles at all concentrations.12 Similarly, C18-tailed amine oxides can also form wormlike micelles at concentrations exceeding about 20 mM.9 Based on these past studies, it is reasonable to expect that an even longer (C22) tailed zwitterionic surfactant such as EDAB would be able to directly assemble into wormlike micelles at very low concentrations. This explains why we find highly viscoelastic rheological behavior for as low as 2.5 mM EDAB in the absence of salt. The zwitterionic nature also explains why the addition of NaCl has no effect on the rheology.

Comparison with EHAC Worms. It is also instructive to compare the results for EDAB with those for C22-tailed cationic surfactants such as erucyl bis-(hydroxyethyl)methyl ammonium chloride (EHAC), which has been studied extensively over the past few years.17,20,22 Being an ionic surfactant, EHAC does not form viscoelastic micellar solutions on its own, but it does so upon addition of salts such as NaCl or NaSal.20,22 In particular, a sample of 60 mM EHAC with 30 mM NaSal has been reported to show the same pattern of rheological behavior as reported here for EDAB.20 That is, the sample showed gel-like behavior at low temperatures (25–60 °C) and a viscoelastic, Maxwellian response at higher temperatures. Moreover, the zero-shear viscosities of this EHAC/NaSal sample were reported to be very high ($\eta_0 > 10$ Pa.s) at temperatures exceeding 75 °C20 the same is true for the EDAB solutions studied here. These high viscosities suggested that EHAC worms were exceptionally long,20 and again the same conclusion should apply for EDAB worms as well. It is clear that the common thread to both EDAB and EHAC is the C22 tail. The question then is why (or how) such a long
surfactant tail leads to the distinctive rheological response of the micelles, including their gel-like behavior at low temperatures.

Connection Between Gel-Like Response and Micellar Breaking Time. We believe the crucial factor to be the breaking time \( t_B \) of the micelles, and we hypothesize that long surfactant tails lead to very long breaking times. The breaking time refers to the time it takes for a micellar chain to break in two due to the exchange of unimers with other micelles. As discussed earlier, the characteristic Maxwellian response of wormlike micelles occurs in the fast-breaking limit, where the micellar breaking time \( t_B \) is much less than their reptation time \( t_{rep} \). From the literature, this assumption appears to be valid for worms based on C16-tailed surfactants at all temperatures, and the few existing measurements of micellar breaking times have reported values of \( \sim 10^{-9} - 10^{-1} \) s. In turn, for such C16-tailed surfactant micelles, if the measured relaxation time \( t_B \) of the sample is 50 s, then, using the equation for \( t_B \) in the fast-breaking limit \( (t_B = \sqrt{t_B t_{rep}}) \), we calculate a \( t_{rep} \) of \( \sim 10^5 \) s. On first glance, this appears to be an anomalously large value for \( t_{rep} \), but such values are actually quite reasonable: in essence, \( t_{rep} \) is so high because micellar contour lengths are so large (several micrometers). It is known from polymer theory that \( t_{rep} \sim L^3 \), where \( L \) is the average contour length.

How are the above time scales modified when we go from a C16- to a C22-tailed surfactant? We suggest that the micellar breaking time \( t_B \) is increased by several orders of magnitude. Note that micellar breaking involves an exchange of unimers from one micelle to another. In this process, unimers will have to travel through the aqueous solution, and therefore, their solubility in water will influence the process. Because of their long (C22) hydrophobic tails, we suggest that the breaking of EDAB micelles will be a relatively unfavorable process. Similar arguments are generally used to explain why lipid vesicles in water very rarely exchange lipids between each other; this is presumed to be due to the low solubility of the two-tailed lipids.

Our hypothesis, therefore, is that EDAB micelles will be relatively “unbreakable” at room temperature, and their dynamics will then be determined primarily by reptation, that is, \( t_B \sim t_{rep} \). Assuming that \( t_{rep} \) is at least on the order of \( 10^3 \) s as estimated above, it will mean that the relaxation time \( t_B \) of an EDAB sample at room temperature falls well outside the experimentally accessible window. This would explain why the sample behaves like a permanent gel at low temperatures. As the sample is heated, however, it seems that the gel does eventually revert to a viscoelastic fluid having a finite relaxation time. For example, Figure 3 shows that a 50 mM EDAB sample has a finite \( t_B \) above 60 °C, and moreover, its Maxwellian behavior implies that the micelles are in the fast-breaking regime (\( t_B \ll t_{rep} \) ) at these high temperatures. The drop in \( t_B \) to a finite value is evidently due to a decrease in both \( t_{rep} \) (due to the drop in micellar contour length) as well as \( t_B \). In the case of the breaking time \( t_B \), a decrease with temperature makes sense, since micelles will be able to exchange unimers more easily at higher temperatures. Indeed, a reduction in \( t_B \) with temperature has been observed in experiments, but the functional form of this relationship needs to be studied further.

Our hypothesis of long breaking times for EDAB worms provides a consistent framework to explain our results. Although we are not aware of any systematic studies of micellar breaking time as a function of surfactant tail length, we believe that the postulated trend is sensible. Indeed, surfactant solubility is generally equated with the CMC, and the CMC of a C22-tailed surfactant will be orders of magnitude lower than that of a C16-tailed surfactant. Interestingly also, long breaking times are consistent with a high end-cap energy \( E_c \) of the micelles, and indeed, the \( E_c \) for micelles of the C22-tailed EHAC surfactant has been shown to be particularly high. On a different note, we can also extend the same arguments to explain the rheological behavior of self-assembling biopolymer gels, such as those of F-actin or microtubules. In these cases too, an entangled (non-cross-linked) network of chains shows a permanent gel-like rheology (\( G' \) independent of frequency in dynamic rheology; yield stress and lack of low-shear plateau in steady-shear rheology). Here again, presumably, the chains are very long and exchange of unimers is a rare event (i.e., breaking times are very long).

Discussion of Salt Effects on EDAB Worms. Finally, we consider the reasons why the addition of organic salts such as NaHNC and NaSal reduces the viscosity of EDAB samples. When the same salts are added to cationic surfactants, the viscosity generally goes up as the salts induce the growth of wormlike micelles. Mechanistically, the salt counterions (\( \text{HNC}^- \) and \( \text{Sal}^- \)) bind to the cationic headgroups and thereby reduce their effective charge. We believe that counterion binding also occurs when the salts are added to EDAB, but with a different consequence. Since the counterions are anionic and the headgroups are zwitterionic, counterion adsorption will increase the charge on the headgroup (i.e., it will transform the micelles from zwitterionic to anionic). In turn, headgroups will have a larger effective area, and geometric packing considerations will favor a transition from cylindrical to spherical micelles. This could explain why the EDAB micelles become shorter, leading to a drop in viscosity with salt addition (Figures 8 and 9). Note that counterion adsorption onto EDAB micelles will be driven not by electrostatic interactions, since the headgroups have only a weak charge, but by hydrophobic interactions. Since NaHNC has a bulkier hydrophobic part (Scheme 1), its counterions will adsorb at lower concentrations compared to NaSal. This reasoning explains the results in Figure 9, where NaHNC is found to influence the viscosity at much lower concentrations compared to NaSal.

5. Conclusions

We have demonstrated that the C22-tailed zwitterionic surfactant EDAB forms very long wormlike micelles in water at low concentrations. The unusual result from this study is that EDAB worms can respond as either elastic gels or viscoelastic solutions, depending on the temperature. At low temperatures (25–60 °C), the samples respond like “permanent” elastic gels, whereas at higher temperatures the same samples show the viscoelastic Maxwellian response that is typical of wormlike micelles. We hypothesize that the gel-like behavior arises because EDAB worms are “unbreakable” at low temperatures, that is, their breaking time \( t_B \) is very long (in turn, this is connected with the long C22 tails and the resulting low solubility of EDAB unimers in water). Consequently, the long EDAB worms relax very slowly by reptation, leading to the gel-like behavior. At higher temperatures, the worms become shorter and they rapidly break and re-form like conventional worms, causing the rheology of...
to revert to a more typical viscoelastic response. We have also investigated the sensitivity of EDAB worms to salts: while inorganic salts have no effect, organic salts with hydrophobic counterions such as NaHNC and NaSal reduce the viscosity. We postulate that hydrophobic counterions adsorb onto EDAB micelles and thus impart a net charge to the headgroups. The charge transforms the micelles into smaller entities, which explains the reduction in viscosity.

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