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Elongational Flow Behavior of Cetyltrimethylammonium Bromide/Sodium Salicylate Surfactant Solutions

Y. Hu, S. Q. Wang,* and A. M. Jamieson

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44016

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The elongational flow behavior of cetyltrimethylammonium bromide (CTAB)/sodium salicylate (NaSal) solutions is investigated using a Rheometrics RFX fluid analyzer. For dilute solutions, the elongational stress slowly increases with time upon the application of a constant strain rate and eventually arrives at a fluctuating plateau region, where the elongation viscosity is several orders of magnitude larger than the shear viscosity at a comparable shear rate. The time required for the stress growth is inversely proportional to the strain rate and decreases dramatically with the surfactant concentration. At higher concentrations, the ratio of the elongational to shear viscosities at low strain rates decreases toward the Trouton value of 3. It is suggested that elongational flow promotes side-to-side collisions between micelles which result in micelle growth. Furthermore, the salt (NaSal) concentration is found to be a key variable influencing the micellar self-assembly in both elongational and shear flow fields.

Introduction

The rheology of surfactant solutions under shear flow has been studied extensively. At high concentrations, these solutions show typical viscoelastic behavior.[1-3] At low concentrations, they may show more complex and unusual rheological phenomena such as rheopexy and shear thickening.[4,5] Many studies have been carried out to elucidate the mechanism for the rheopectic and shear thickening phenomena.[6-12] It is now generally accepted that shear-induced micellar association is responsible for these unusual flow behaviors.

Micellar self-assembly under an extensional flow has been theoretically studied recently. Cates and co-workers[13] concluded that elongational flow is more effective in promoting micellar growth than simple shear because the rodlike micelles are better aligned to enhance end-to-end coagulation. A thermodynamic treatment,[14] however, predicted micellar shrinkage in elongational flow on the basis of the argument that the effective free energy per surfactant is less in a short micelle than in a longer one.

Recently, Prud'homme and Warr reported a first elongational flow study on tetradecyltrimethylammonium (TTAB)/sodium salicylate (NaSal) micellar solutions.[15] It was found that these solutions extensionally thicken in a manner similar to that of polymer solutions. Furthermore, at low concentrations the ratio of elongational to shear viscosities is found to be considerably larger than 3. This observation was taken as evidence for enhanced micelle growth in a potential flow.

If micelle growth in elongational flow is firmly established by experiment, one is led to the following profound conclusion: self-assembling fluids cannot be treated within a generalized thermodynamic framework, even for potential flows whose role has been traditionally described by an additional potential energy term in an effective total free energy. This effective potential approach, advocated first by Kramers,[16] evidently does not account for any effect of flow convection on the molecular structure of the fluids. It is conceivable that the elongational flow convection is important and can influence micelle self-assembly and increase the micelle sizes. Micelle coagulation could be enhanced by a uniaxial elongational flow along the "radial" direction perpendicular to the flow direction. In other words, for anisotropic particles such as rod-to-wormlike micelles that are aligned in the flow, side-to-side collisions may take place, but not end-to-end collinear collisions.

Here we study the elongational flow properties of aqueous cetyltrimethylammonium bromide (CTAB) solutions as a function of the CTAB concentration and the sodium salicylate (NaSal) salt concentration. Our previous work[11] has shown that the NaSal to CTAB ratio controls the micellar lifetime and therefore determines the micelles' ability to grow under the influence of shear. A similar effect is found for the micellar solutions in elongational flow. Our results provide further evidence suggesting that a uniaxial extensional flow may strongly promote micellar self-assembly far beyond that achieved in the quiescent state. Therefore, a Kramers type thermodynamic treatment[14,16] of flow effects on self-assembling systems is shown to be unreliable.

Experiment

Materials. Cetyltrimethylammonium bromide from Sigma Chemicals and sodium salicylate from Aldrich Chemical were used. The solvent was distilled water. All the samples were equilibrated at 80 °C for 1 day and then at room temperature for at least 1 more day. All the measurements were made at 25 °C, unless otherwise specified.

Methods. The Rheometrics Fluid Spectrometer RFS 8500 in cone and plate geometry (50 mm diameter, 0.02 rad cone angle) was used for steady and oscillatory shear viscosity measurements. Elongational viscosity measurements were performed using a Rheometrics RFX Fluids Analyzer. The RFX produces a localized elongational flow by immersing two opposing nozzles in the sample from which the fluid is sucked into two motor driven syringes. The fluid passing through the two opposing nozzles is not returned to the sample beaker. Both the nozzle diameter and separation are 4 mm.

Results and Discussion

We first characterized some standard Newtonian fluids to determine the accuracy of the elongational rheometer. Figure 1 shows the elongational viscosities of two glycerol/water mixtures having glycerol:water ratios of 4:1 and 5:2, respectively. The corresponding shear viscosities were determined to be 0.81 P for the 4:1 mixture and 0.38 P for the 5:2 mixture using the Rheometrics RFS 8500. Evidently the elongational viscosities are approximately 3 times the shear viscosities when the elongation strain rate is below 300 s^{-1}; i.e. the Trouton law is observed to hold for both mixtures. Above 300 s^{-1}, the elongational viscosity increases slightly with the strain rate, presumably due to the

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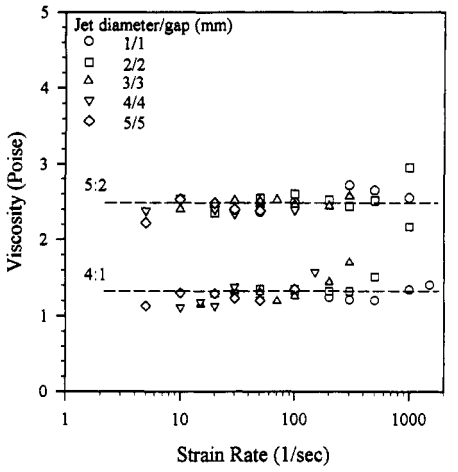


Figure 1. Elongational viscosities of two glycero/water mixtures (4/1 and 5/2) measured with different jet sizes at 22 °C. The shear viscosity of the mixture is 0.81 for the 4/1 mixture and 0.38 for the 5/2 mixture.

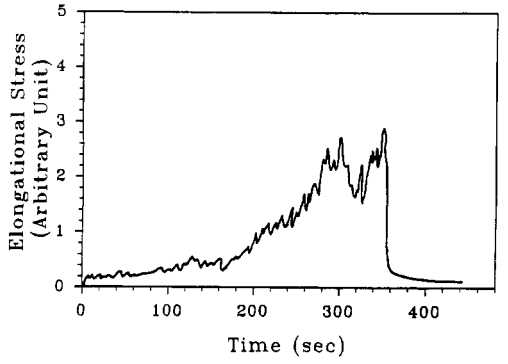


Figure 2. Elongational stress growth and relaxation for a 2 mM CTAB and 2 mM NaSal mixed solution. An elongational strain rate of 2 s^{-1} is applied for 360 s and then terminated.

kinetic energy effect. In our study of CTAB/NaSal micelles, the strain rates are confined to within 200 s^{-1} so that the kinetic effect is negligible.

Figure 2 shows a typical stress growth and relaxation curve after a constant elongational strain rate of 2 s^{-1} is applied to a 2 mM equimolar CTAB/NaSal solution. The stress increases slowly and eventually reaches a plateau region where it fluctuates vigorously. The duration of the stress growth is more than 200 s, which seems to be surprisingly long. Although the micellar solution is not recirculating during the measurement, the residence time of the sample does vary with position (see Figure 9). The time T required to move from a certain position z_1 to another position z_2 along the z axis is

$$T = \frac{1}{\dot{\epsilon}} \ln\left(\frac{z_2}{z_1}\right) \qquad (1)$$

where $\dot{\epsilon}$ is the elongation rate. There is a stagnation point at the midpoint where $x, y, z = 0$. Fluid elements close to the stagnation plane may take a long time to reach the nozzle. Thus micelles can continue to build up near the midplane, producing higher elongational stress, as seen in Figure 2.

The transient flow behavior of the more concentrated solutions varies with the strain rate as shown in Figure 3. The stress grows smoothly to a plateau at a low strain rate and experiences an overshoot at an intermediate strain rate. When the strain rate is sufficiently high, the stress fluctuates vigorously at the plateau region. Prud'homme et. al.[15] reported similar behavior for TTAB/NaSal solutions. In comparison, the glycerol/water mixture does not show any stress growth and fluctuation at strain rates up to 100 s^{-1}, indicating that the temporal variation of the observed stress growth in the micellar solutions is not an artifact. For all

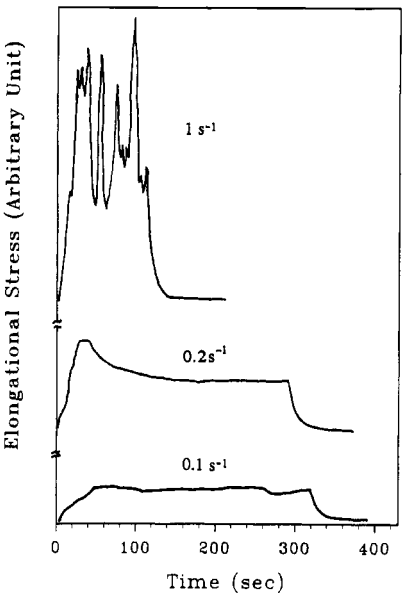


Figure 3. Elongational stress growth and relaxation for a 20 mM CTAB and 30 mM NaSal mixed solution at different strain rates.

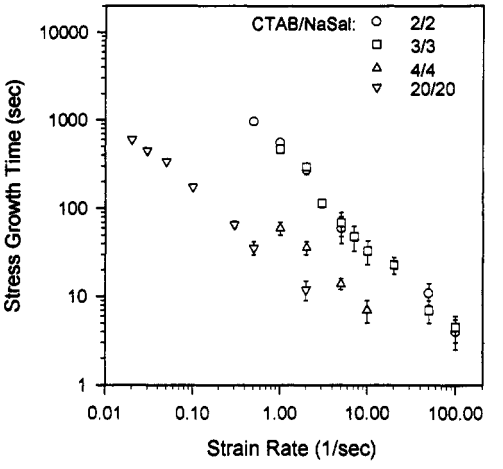


Figure 4. Time required for the stress to reach the plateau as a function of strain rate for solutions with different CTAB:NaSal concentrations.

the micellar solutions, the time required to reach the plateau decreases with increasing strain rate and the surfactant concentration, as shown in Figure 4. It appears that the time is inversely proportional to the average strain rate; i.e. a constant strain is required to reach the plateau viscosity for a given solution. The critical strain decreases dramatically with increasing surfactant concentration. The inverse relation between the stress growth time and the strain rate is evidently consistent with eq 1, even though the actual strain rate and residence time are not constant from place to place. It appears that, despite the complex nature of the elongational flow field, the strain rate retains its physical significance, as in the case of a Newtonian fluid.

The average elongational viscosity at the plateau region is plotted against the strain rate and compared with the corresponding values of the shear viscosity for different surfactant concentrations, as shown in Figure 5 to Figure 8. As a cautionary note, since the fluid experiences a complex strain history prior to reaching the nozzle, it should be realized that the magnitude of the elongational viscosity at a specified strain rate may not fully reflect the effect of that particular strain rate. However, the viscosity change with respect to strain rate or sample parameters should be at least qualitatively correct. For the 2 mM equimolar CTAB/NaSal solution, the elongational viscosity is over 3 orders of magnitude higher than that of the shear viscosity at the corresponding shear rate, as shown in Figure 5a. Such an

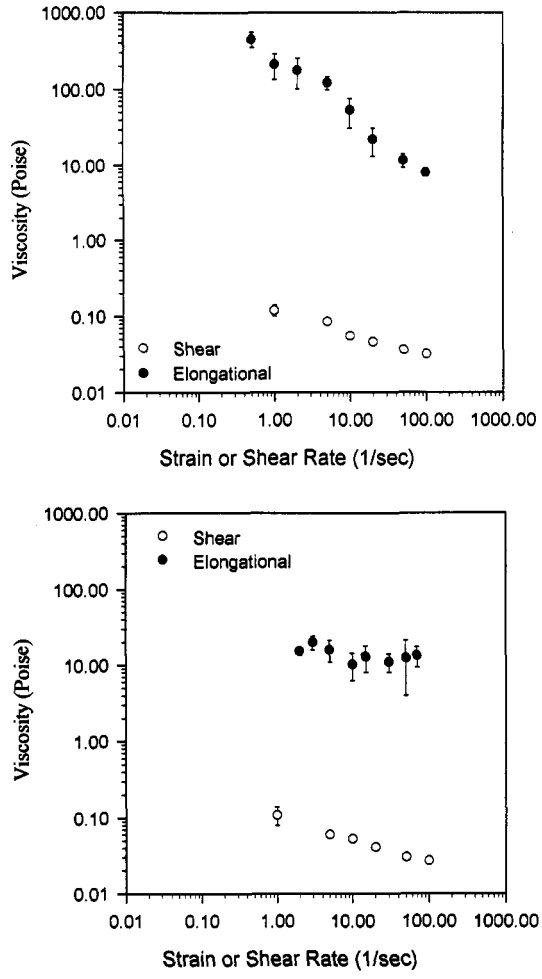


Figure 5. Plateau elongational viscosity at different strain rates compared with the steady shear viscosity at corresponding shear rates for solutions of 2 mM CTAB containing (a, top) 2 mM and (b, bottom) 3 mM NaSal.

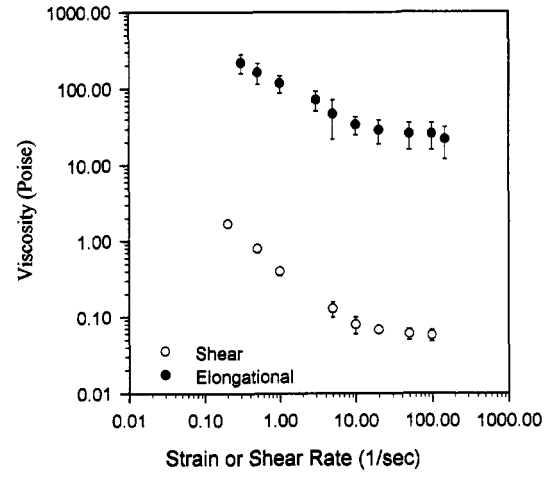
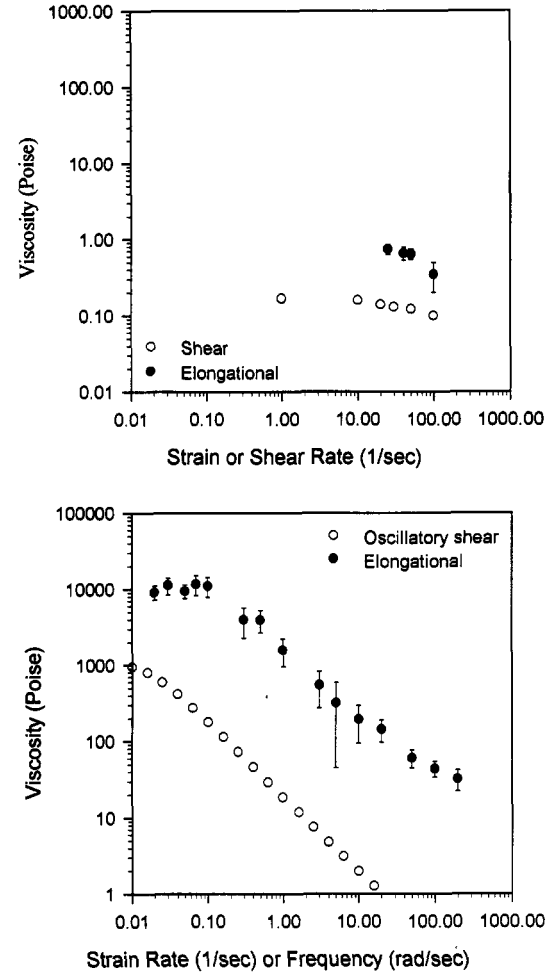


Figure 6. Plateau elongational viscosity at different strain rates compared with the steady shear viscosity for a 5 mM equimolar CTAB/NaSal solution.

enormous difference must arise from structure buildup in the micellar solution due to the influence of the elongational flow. Micellar growth in elongational flow is also consistent with the presence of a long stress growth time and its inverse relationship with the strain rate, as shown in Figure 2 and Figure 4. It is interesting to note that at 2 mM the NaSal to CTAB molar ratio strongly affects the magnitude of the elongational viscosity as evidenced by a comparison between Figure 5a and 5b. This is in agreement with the previously established result that the micelles have the longest lifetime around the unit NaSal/CTAB



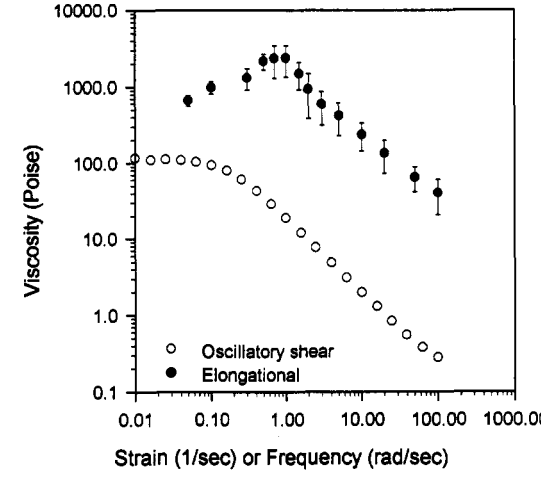


Figure 7. Plateau elongational viscosity at different strain rates compared with the steady or oscillatory (γ = 5%) shear viscosity for solutions of 20 mM CTAB containing (a, top) 10 mM, (b, middle) 20 mM, (c, bottom) 30 mM.

ratio.[11] For an equimolar solution of NaSal/CTAB at the concentration 5 mM, a difference of 2 orders of magnitude between elongational and shear viscosities is observed as shown in Figure 6. Figure 7a–c presents the elongational and shear viscosities as a function of strain rate for three different salt-to-surfactant molar ratios at a 20 mM CTAB concentration. Figure 7a indicates that at NaSal/CTAB = 1/2 the micelles are rather small despite the relatively high concentration, and they remain small under the influence of the elongational flow because of their short lifetime. When the NaSal/CTAB ratio increases to unity, both shear and elongational viscosities increase nearly 4 orders of magnitude, as shown in Figure 7b. Note that oscillatory shear

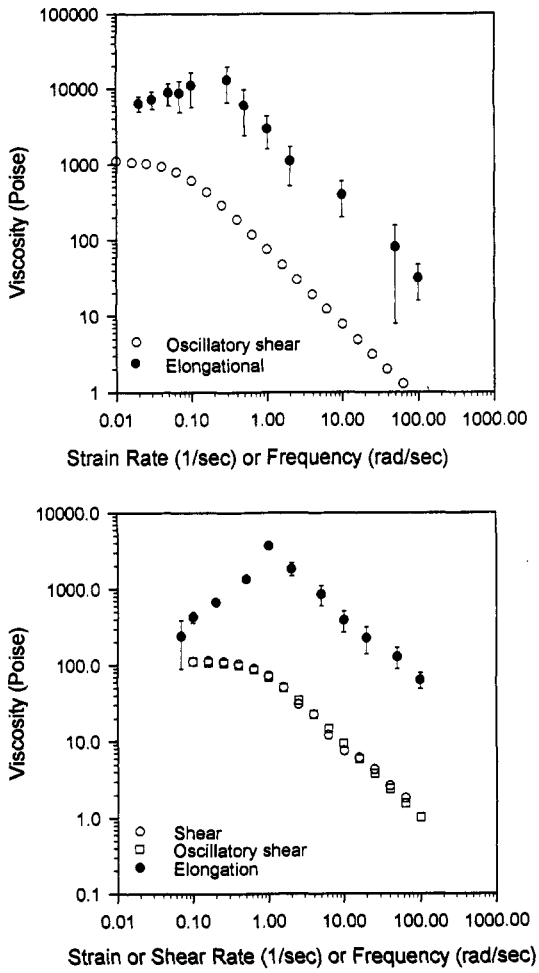


Figure 8. Plateau elongational viscosity at different strain rates compared with the steady or oscillatory (γ = 5%) shear viscosity for solutions of 40 mM CTAB containing (a, top) 40 mM and (b, bottom) 60 mM NaSal.

with a 5% strain amplitude was used for convenience and to avoid viscoelastic flow instabilities at high shear rates.[17]

It is important first to point out that the 20 mM equimolar NaSal/CTAB solution (Figure 7b) shows only 1 order of magnitude difference between elongational and shear viscosities, as compared to 3 orders of magnitude at 2 mM (Figure 5a) and 2 orders of magnitude at 5 mM (Figure 6). Upon a further increase of the NaSal concentration to a NaSal/CTAB ratio equal to 30/20, both shear and elongational viscosities decrease roughly 1 order of magnitude (Figure 7c), corresponding to a break-up into shorter micelles with additional salt. From previous work,[3,11] we can infer that the micellar lifetimes becomes shorter at high NaSal/CTAB ratios. The solution is nearly Newtonian at small rates of strain, and the elongational viscosity is only several times the shear viscosity.

The behavior of a 40 mM equimolar NaSal/CTAB solution is very similar to that of the 20 mM equimolar solution as shown in Figure 8a. Increasing the NaSal concentration to 60 mM has the enormous effect of reducing both shear and elongational viscosities by 1 order of magnitude, as shown in Figure 8b. The same salt effect can be seen by comparing Figure 7b with Figure 7c.

The stress growth as shown in Figure 2 under elongational flow resembles that under shear flow.[11] Such rheopectic behavior has been studied in shear flow and interpreted as flow-induced coagulation. In a simple shear flow $\vec{u} = \dot{\gamma} y \vec{x}$, there is a velocity gradient perpendicular to the flow direction. Micelles in different stream lines may collide with each other in the flow direction and combine to grow in size. In a uniaxial elongational flow field defined by $\vec{u} = \dot{\epsilon}(z\vec{z} - 0.5x\vec{x} - 0.5y\vec{y})$, micelles accelerate in the

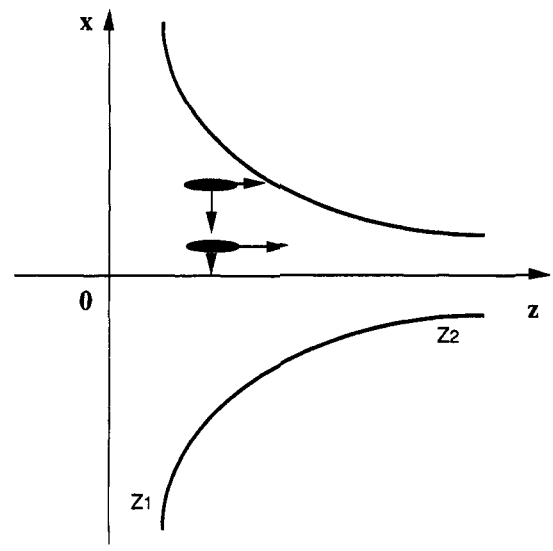


Figure 9. Schematic picture of micelles in motion under uniaxial elongational flow field.

flow direction but decelerate in the x and y directions, as depicted in Figure 9. The flow-aligned micelles may therefore undergo side-to-side collisions along the radial direction. Micelles may grow in size after collisions through a "fusion" mechanism similar to that which occurs under shear flow. As a result, longer micelles or larger micellar networks can be formed, leading to a much larger elongational viscosity. Such a kinetic mechanism is indeed supported by all our observations. The enormous plateau elongational viscosity relative to the shear viscosity (as shown in Figure 5) is unequivocal evidence for the presence of micellar structures which are much larger than the equilibrium micelles whose sizes are reflected in the magnitude of the shear viscosity. The large plateau elongational viscosity relative to the initial one and the extraordinarily slow elongational stress relaxation indicated by the long decaying tail in Figure 2 offer further evidence for formation of unusually large micellar structures due to elongational flow convection. At comparable rates, the shear stress relaxes instantaneously, implying that the equilibrium micelles are originally much smaller than those formed in the elongational flow.

Like the shear thickening phenomenon, the magnitude of elongational thickening decreases as the surfactant concentration increases. This is indicated by the diminishing difference between the elongational and shear viscosities with increasing surfactant concentration. Similar trends have been observed by Prud'homme and Warr.[15] This behavior is obviously inconsistent with imterpreting the phenomenon as due to stretching of micellar conformations. The sharp decrease of the elongational to shear viscosity ratio, as the surfactant concentration increases from 2 to 40 mM, simply indicates that micelles cannot grow much longer than their equilibrium sizes at sufficiently high concentrations.

Our study of the salt effect shows that a short micellar lifetime inhibits any micellar growth in elongational flow. It is interesting to compare Figure 7a with Figure 5b, corresponding to 20 mM CTAB/10 mM NaSal and 2 mM CTAB/3 mM NaSal solutions, respectively. Each solution has a similar shear viscosity. Judging by the magnitude of their elongational viscosities, the 20 mM solution did not experience significant micellar growth under the influence of elongational flow, whereas the 2 mM solution formed much larger micellar structures under identical flow conditions. We can infer from previous work[3] that the 20 mM solution with such a low NaSal/CTAB ratio probably contains very short-lived micelles that cannot grow much larger in flow because they break up so frequently. In this case even the elongational flow is not very effective in altering the micellar solution structure, and the elongation viscosity is only about 3 times the shear viscosity.

Conclusion

This present study supports a previous conclusion[15] that elongational flow can promote micellar growth. For dilute solutions of CTAB and NaSal we found the elongational stress increases with time upon the application of a constant strain rate and eventually reaches a fluctuating plateau region, where the elongation viscosity is several orders larger than the shear viscosity at a comparable shear rate. The stress growth period is long and inversely proportional to the strain rate. It is proposed that elongational flow produces side-to-side collisions between micelles as the flow converges radially toward the symmetry axis, and that micelles grow in size after collisions through "fusion", resulting in stress growth and a much larger elongational viscosity than the shear viscosity. The tendency for micellar growth decreases with increasing surfactant concentration. The NaSal/CTAB ratio has a similar influence on the equilibrium and thickening states and for elongational and shear flow fields. The elongational and shear viscosities are each highest near unit NaSal/CTAB ratio, i.e. at charge stoichiometry. Similar effects of salt have been observed previously on shear flow properties of micellar solutions.[11]

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