Shear-Induced Vesicle to Wormlike Micelle Transition

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The present paper reports the first observation of a vesicle to wormlike micelle transition in the surfactant cetyltrimethyl ammonium 3-hydroxynaphthalene-2-carboxylate induced by shear. The structural aspects investigated by small angle neutron scattering indicate that the transition induced by shear, temperature, and added surfactant present similar aspects. Step-shear experiments indicate the presence of other shear-induced transitions with very long characteristic times.

Spontaneously formed surfactant structures represent interesting systems and in the recent years have emerged as an important group of advanced materials.[1] The two structures of relevance in the present context are vesicles and wormlike micelles. Vesicles are closed bilayers or multilayers of surfactants and are of great industrial importance as encapsulating agents for the controlled release of drugs and perfumes in formulations.[2] Wormlike micelles are very long and flexible. They are of interest because of their complex rheology and are used in drag reduction, thickening chemical formulations, etc.[3] Transformation of vesicles into micelles and vice versa occurs in nature during the digestion process[4] and also in biochemical studies involving membrane reconstitution.[5]

In the present paper we report the effect of shear on systems containing coexisting vesicles and micelles. Some rheologically induced phase transitions in surfactant systems are known,[6] but to our knowledge, this is the first time that a vesicle to micelle transition induced by shear is reported.

The main surfactant chosen is cetyltrimethyl ammonium 3-hydroxynaphthalene-2-carboxylate (CTAHNC), which can be looked upon as a complex of two oppositely charged surfactants—CTA^+ and HNC^-. The system, as we shall see below, has the unique feature of being able to undergo a transition from vesicle to micelle phase in three different ways, namely, increase in temperature,[7] addition of a surfactant,[8] and on shearing. We investigate these transitions using small angle neutron scattering (SANS) and rheology.

CTAHNC was prepared by a method reported earlier,[8] and CTAB was obtained from Sigma Chemicals. SANS experiments were performed on spectrometer PAXY at Laboratoire Léon Brillouin at Saclay, France. The spectrometer configuration was sample−detector distance = 4 m and incident wavelength = 10 Å. Standard data treatment procedure was applied to raw data. The rheological experiments were performed on a Rheometrics RFS II fluid spectrometer using couette geometry.

The main characteristics of temperature-induced vesicle to micelle transition in a 12 mM CTAHNC are that the turbid vesicle phase with low viscosity (~0.1 Pa·s at 30 °C) containing vesicles of diameter 1−10 μm gets transformed into an optically clear micellar phase that contains wormlike micelles and is strongly viscoelastic. These characteristics have been determined using optical microscopy, NMR, fluorescence anisotropy, light scattering, and rheology.[7,8] The transition has a width of about 20° around 50 °C with coexisting vesicles and wormlike micelles.

The vesicle to micelle transition in CTAHNC can also be induced by adding surfactants such as CTAB, Triton X-100, and SHNC.[7,8] Video microscopy experiments have revealed that the addition of CTAB to 12 mM CTAHNC at 30 °C induces a disparition of vesicles for [CTAB] > 2 mM.[8] The optical micrograph for 12 mM CTAHNC with 0.5 mM CTAB showed vesicles of smaller diameter ~2 μm with reduced polydispersity. The reduction in size of the vesicles is the precursor for wormlike micelles brought forth by this transition.

Step-shear method was applied to observe nonlinear effects in these systems. In this method, a constant shear rate $\dot{\gamma}$ is applied and the stress (σ) is continuously monitored. After equilibration at one shear rate, a step increase in shear is introduced and the approach to a new equilibrium is monitored. The first experiment with step shear method was done at 60 °C on CTAHNC 12 mM with CTAB 0.5 mM. At this temperature we expect only wormlike micelles in the system.[8] The second experiment was done on the same system and for an identical sequence of shear rates but at 35 °C. This sample consisted of vesicles as confirmed by optical micrograph and a small fraction of micelles. The samples were equilibrated at each temperature for 30 min before starting the experiment. For both experiments four shear rates 0.1, 2.0, 9.0, and 16.0 s^{-1} were applied for periods of 20, 10, 10, and 10 min, respectively. The stress was monitored every 2 s.

Traces A and B in Figure 1 show the results of the first and second experiments, respectively. Both traces A and B consist of two regions in the first shear step. Region I of trace A corresponds to initial rise in stress in the first 10 s, hardly seen on the figure due to the scale used. This initial rise is followed by region II, that is, a stress relaxation with a characteristic time of the order of 100 s until a stationary value is achieved. When the shear rate is further increased, the behavior of the stress is the same: an increase followed by a relaxation to another equilibrium value that is very close to the previous one. Such an equilibrium value is almost shear rate independent, and it is a signature of a nonlinear behavior as observed in other wormlike micelles.[9,10] In this domain, an instability develops

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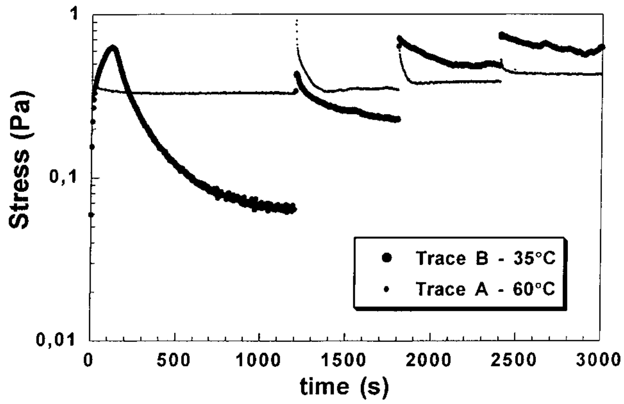

Figure 1. Stress vs time for CTAHNC 12 mM with CTAB 0.5 mM at 60 °C (trace A) and at 35 °C (trace B) in the step-shear method. The shear rates used were 0.1, 2.0, 9.0, and 16 s^{-1} applied for 20, 10, 10, and 10 min, respectively.

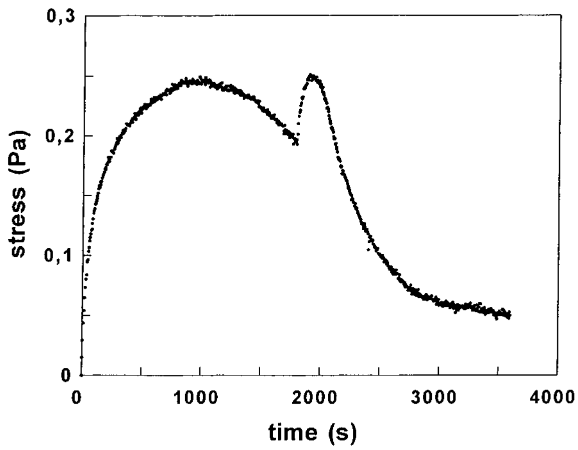

Figure 2. Stress vs time for CTAHNC 12 mM with CTAB 0.5 mM at 35 °C in the step-shear method. The shear rates used were 0.02 and 0.06 s^{-1} applied for 30 min each.

involving the coexistence between a phase of aligned micelles and a more viscous phase of nonoriented micelles. This behavior is not yet fully understood, but both theoretical and experimental studies show that the equilibrium stress exhibits a plateau, σ_m, or a quasi-plateau as a function of shear rate.[9,11,12] This is indeed observed for the trace A of Figure 1. The onset of this nonlinear behavior is predicted to be at $\dot{\gamma} = 2.6\ \tau_R^{-1}$, where τ_R is the terminal time of the stress relaxation.[12] Oscillatory experiments performed on sample of trace A show that τ_R is of the order of 17 s, leading to $\dot{\gamma} = 0.15$, very close to the experimental value of $\dot{\gamma} = 0.1$ for the first step of Figure 1. Furthermore, the theory[12] predicts that $\sigma_m / G'_\infty = 0.67$, where G'_∞ is the plateau modulus. For this system it was found that $G'_\infty = 0.8$ Pa, which leads to $\sigma_m/G'_\infty = 0.54$. We also found, using the rate sweep method (with shear rates varied from 0.02 to 100 s^{-1} in 5 steps per decade and data collected for 50 s for each shear rate), $\sigma_m = 0.55$ Pa, leading to $\sigma_m/G'_\infty = 0.7$. These values are not too far from the predicted ones. Concerning the long time necessary to reach the equilibrium, there is not at present any quantitative description.

As for the behavior of the system where vesicles and micelles coexist, it is qualitatively the same (trace B), but the relaxation times involved are much longer since the rise time is of the order of 200 s for the first step and the decay time seems to be as long as 20 min. We doubt that this behavior, which is observed even at smaller shear rates (Figure 2), is linked to the vesicle to micelle transition, but we rather think that it is due to the development of an instability involving layered flow of

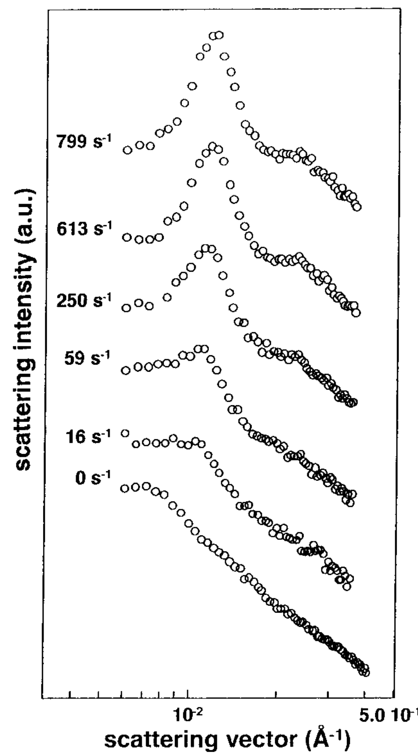

Figure 3. Scattered intensity as function of the scattering vector in log−log scale for various shear rates. The sample is CTAHNC 12 mM with 0.5 mM CTAB at 37 °C.

the vesicle and the more viscous micellar phase. Rheooptical experiments would be necessary to elucidate this phenomenon.

At high shear rates the stress for both traces A and B approach each other, indicating possibly that the system at 35 °C might be converted to micelles by shearing. The behavior is similar to that at 60 °C where one has only wormlike micelles.

Next we turn to structural investigations using SANS to check some of the above conclusions. The experiments were done with a two-dimensional detector, and each spectrum was counted for 1 h. Data were grouped in circular sectors of 10° in directions parallel and perpendicular to the flow. The concentration of CTAHNC was 12 mM and that of CTAB 0.5 mM, and the temperature was 37 °C. The sample under these conditions consists of vesicles and a small fraction of micelles, and its scattering for zero shear rate exhibits a very small peak at very small angles.

In Figure 3 is displayed the scattered intensity vs q in log−log scale. The direction of q shown in the figure is perpendicular to the flow. In parallel direction no correlation peak is observed, and the scattered intensity decreases as the shear rate increases. The asymmetry observed in the two directions indicates the alignment of micelles. Three main features can be observed in Figure 3:

(a) A very sharp peak develops with increase in shear rate;

(b) At shear rates above 59 s^{-1} a second-order peak emerges;

(c) The first-order peak clearly moves to higher values of q with shear rate.

Features a and b have been observed in shear experiments on wormlike micelles[13] since the first report[14,15] and have been investigated in quantitative details. These features have been attributed to shear alignment of wormlike micelles. Feature c, the displacement of the peak to higher q values with increasing shear rates, indicates structural changes in the system with shear and cannot be attributed only to the alignment of micelles in the flow direction.

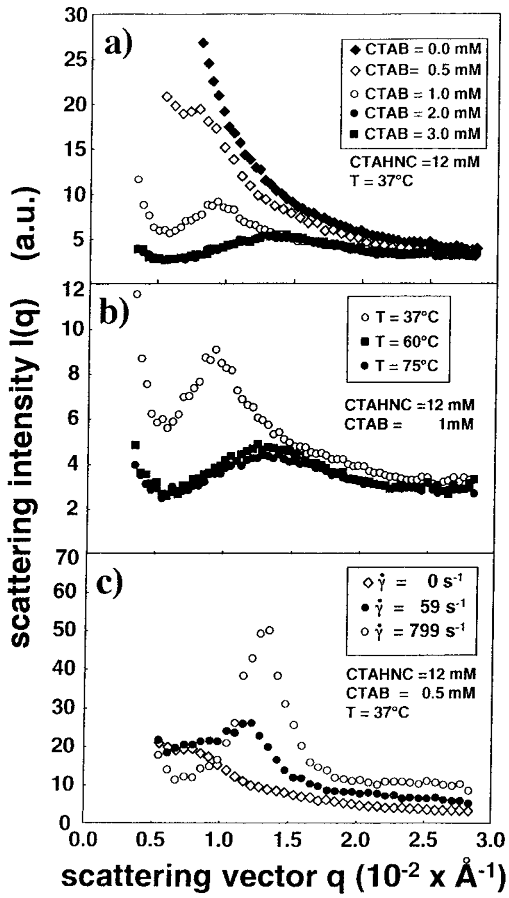

Figure 4. SANS results indicating the transition induced by three routes—CTAB addition (a), temperature increase (b), and shear (c). Note that the final peak position is the same in parts a, b, and c, indicating the conversion of most vesicles to micelles.

From Figure 3, one can observe an initial increase and subsequent saturation in the peak position, q^*, with shear rate, beginning at 0.008 $Å^{-1}$ for $\dot{\gamma} = 0$ and saturating at 0.013 $Å^{-1}$ for $\dot{\gamma} \geq 250$ s^{-1}. The value of q^* is a measure of the volume fraction of micelles. $2\pi/q^*$ gives the average distance between the micelles, and thus q^* is proportional to $\phi^{1/3}$, where ϕ is the volume fraction of the micelles. Increase in q^* is therefore an unambiguous proof of the increase in micellar volume fraction in the sample. Sharpening of the peak indicates the increased ordering of the micelles and the appearance of second-order peak is a manifestation of this fact. Thus the SANS results show increase in volume fraction as well as alignment of the wormlike micelles produced from the vesicle to micelle conversion by shear especially at higher shear rates.

Figure 4 summarizes SANS report on the effect of CTAB addition, temperature increase, and shear on a solution of CTAHNC 12 mM. Figure 4a shows the scattered intensity vs wave vector q at 37 °C. It can be seen that without any CTAB additive there is *no* correlation peak and the scattered intensity reflects the presence of the flat structures of vesicles at those length scales, with $I(q) \sim q^{-2}$. With the addition of CTAB 0.5 mM, a semblance of a correlation peak appears at a q value of about 0.008 $Å^{-1}$. With increase in CTAB concentration the peak position moves to higher values of q, indicating increase in concentration of wormlike micelles. Also, a strong decrease of intensity at very small angles suggests that the volume fraction of vesicles decreases when CTAB is added. At about 2 mM CTAB, most of the vesicles seem to be converted into micelles with no further shift in the peak position for concentrations of CTAB beyond this value. Optical microscopy and rheological results have confirmed this observation.[8]

Figure 4b shows results similar to Figure 4a but this time with rise in temperature for a sample of 12 mM CTAHNC with 1 mM CTAB. At 37 °C this sample consists of a larger fraction of micelles coexisting with vesicles, and a correlation peak is already observed. With increase in temperature, the peak position moves, and at 75 °C it reaches a position identical to the one observed for a sample of 12mM CTAHNC with 3mM CTAB, at 37 °C. It has been shown that beyond 60 °C this system, namely, 12 mM CTAHNC with or without CTAB additive, consists of micelles only.[8]

Figure 4c shows the effect of shear on vesicles in a sample of 12mM CTAHNC with 0.5 mM CTAB at 37 °C as observed in perpendicular direction to the flow. As discussed earlier (Figure 3) the peak moves toward high values of q, saturating for high shear rates with a final position that is the same as that in Figures 4a,b. This is a strong indication that almost all vesicles are transformed into micelles with shear. Note also that for high shear rates, at very small values of q, the scattered intensity is *smaller* than that of the isotropic case. This is also a strong indication of structural changes brought forth by shear at large length scales.

In summary, we have observed a vesicle to wormlike micelle transition induced by shear. Such a transition is found to be identical to the one induced by temperature increase or CTAB addition on the same system. Rheological experiments at very low shear rates reveal the presence of a shear-induced phase transition that requires further investigation.

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