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Rings and loops in perflurosurfactants viscoelastic solutions

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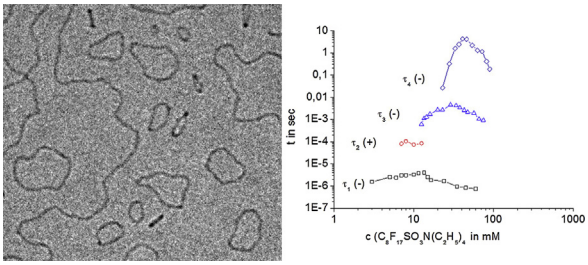
HIGHLIGHTS

- In perfluorosurfactants, electric birefringence detects 4 relaxation times around the 2nd CMC, the onset of the viscosity peak in micellar solutions.
- Cryo-TEM correlates this complex behavior with the formation of small micellar rings and loops, an effective way to avoid micellar endcaps.

GRAPHICAL ABSTRACT



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ABSTRACT

The structure of micellar solutions has been a topic of intense research. Of particular interest is the relation between rheological properties and the nanostructure of the corresponding micelles. At compositions surrounding the 2nd CMC, the onset of micellar growth, spherical micelles typically transition into short rodlike micelles, and these assemblies continue to grow into long, entangled threadlike micelles, avoiding micellar ends. Another possibility to avoid unfavorable micellar ends is to form small closed structures—rings and loops. Here, we disclose with cryo-TEM the formation of these assemblies near the 2nd CMC, for a perfluorosurfactant $C_8F_{17}SO_3N(C_2H_5)_4$, and we correlate the observations with electric birefringence (EB) data that show 4 separate processes near that critical composition.

1. Introduction

Many surfactants form highly viscoelastic solutions already at low surfactant concentrations. Cryo-TEM, SANS and SAXS measurements have shown that such solutions contain elongated micelles called wormlike or threadlike micelles. The elastic properties are due to the formation of an entanglement network of the linear threadlike micelles. The rheological behavior of many such systems has been studied in detail [1–6]. It was established that they often behave like Maxwell fluids, meaning that the zero-shear viscosity η° is given by the product of the shear modulus and the structural relaxation time [7].

$$\eta^\circ = G^\circ \times \tau_s \quad (1)$$

With increasing concentration η° rises usually from the water viscosity, continuously, over many orders of magnitude according to a power law equation

$$\eta^\circ \sim (C/C^x)^\alpha \quad (2)$$

having a high power law exponent α of around 10 [7]. This was also found for the $C_8F_{17}SO_3N(C_2H_5)_4$, a commercially available anionic perflurosurfactant.

This surfactant has a CMC of around 1 mM. Conductivity data showed that the tetraethylammonium counter-ions bind strongly to the micelles [8]. The zero-shear viscosity begins to rise strongly

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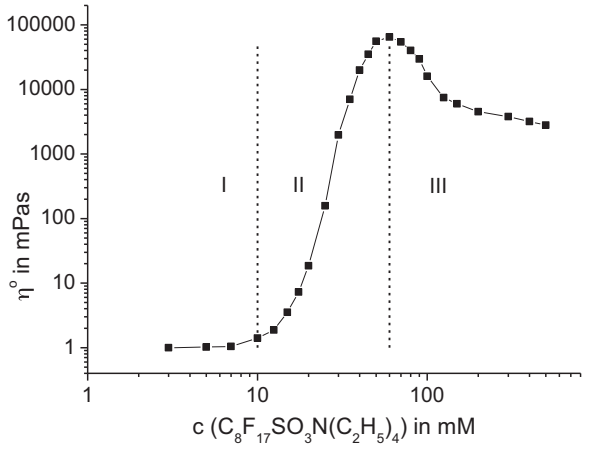

Fig. 1. Zero-shear viscosity of $C_8F_{17}SO_3N(C_2H_5)_4$ aqueous solutions as a function of concentration at $T = 25\,^{\circ}C$.

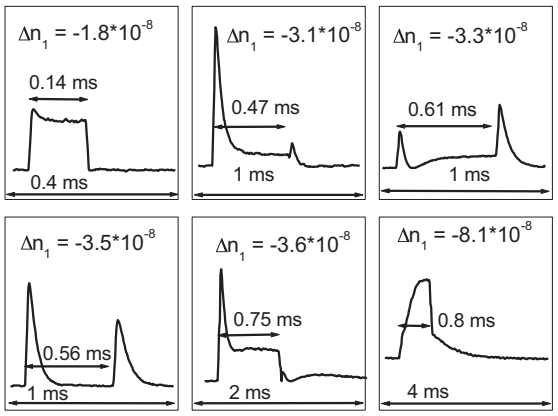

Fig. 2. EB signals from $C_8F_{17}SO_3N(C_2H_5)_4$ at constant field $E = 11.9 \times 10^4\,Vm^{-1}$ at 25 °C for increasing concentrations of (from top left to bottom right): 5, 8, 10, 12, 13 and 14 mM. Pulse lengths (0.14 ms to 0.8 ms) are indicated by arrows to show when the E-field was switched on and off, respectively.

after the 2nd CMC [9–11], the concentration where spherical micelles transition to rodlike; this occurs at around 7.5 mM (Fig. 1, the onset of the viscosity rise) [12]. With further increase in the concentration (region II in Fig. 1) the zero-shear viscosity increases more than four orders of magnitude, and passes over a maximum at 60 mM. The increase is thought to be due to continuous elongation of the wormlike micelles, and the formation of a network of linear, entangled micelles [13]. The power-law increase begins around the overlap of the small rodlike micelles. At further increase, a decrease in the viscosity is observed (region III in Fig. 1), generally attributed to mechanisms such as the formation of branched micelles (see [1], and references therein), or a decrease in the micellar size [14].

In this work, we focus on the onset of the viscosity rise, namely, the region of transition from spherical to elongated micelles. Two experimental methods are combined: electric birefringence (EB), and direct-imaging cryo-transmission electron microscopy (cryo-TEM). The first method can provide information on the length of the micelles at the overlap concentration [12]. The measurements were reported previously but they turned out to be surprising, and could not be well explained. Thus, in this work a correlation with cryo-TEM is used to show directly the structural building units at the transition zone for explaining the unexpected behavior identified in the EB measurements.

2. Experimental

2.1. EB measurement

Experiments were done at the quadratic mode at a constant field $E = 11.9 \times 10^4$ V/m, at 25 °C, and constant laser wavelength of 632 nm, at concentrations around the onset of the viscosity rise, namely, between 5 mM and 14 mM. High-voltage pulses of short rise and decay times were applied, and the time constant of the decay, and the amplitude of the stationary value, were measured.

2.2. Cryo-TEM analysis

Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) always at a controlled temperature (25 °C) and at saturation. A 6 μl drop of the suspension was placed on a 400-mesh TEM copper grid covered with a perforated carbon film. To remove excess solution and produce a thin liquid film the drop was blotted manually. The blotted samples were allowed to stand in the CEVS for 10 s to relax from shearing effects caused by the blotting. The relaxed samples were then plunged into liquid ethane (−183 °C) to form vitrified specimens and transferred to liquid nitrogen (−196 °C) for storage. Vitrified specimens were examined at temperatures below −175 °C using a Gatan 626 cryo holder either in a Tecnai T12 G2 TEM (FEI, Netherlands) or a Philips CM120 TEM operating at 120 kV. Images were recorded on a Gatan MultiScan 791 camera or Gatan UltraScan 1000 using the DigitalMicrograph software (Gatan, U.K.) in the low-dose imaging mode to minimize beam exposure and electron-beam radiation damage, as described [15,16].

3. Results and discussion

EB measurements were performed at 6 concentrations between 5 and 14 mM surfactant, from below the 2nd CMC to way pass it, where the micelles are expected to be already long (see Fig. 1). Specifically, it was expected that a rotation time could be observed according to the equation for τ which would increase as

$$\tau_{rot} = \frac{4\eta l^3}{k_B T} \quad (3)$$

However, within this concentration range in which the viscosity was measured, four separate processes were detectable [12].

Typical signals are shown in Fig. 2. A simple signal was observed only in the very dilute concentration region. This relaxation process τ_1 was associated with the rotation of the small rodlike micelles. However, unexpectedly, the time constant did not increase in time, and instead a second process was noted. Both processes could be measured over an extended concentration region. Finally, at the concentration at which the viscosity began to rise strongly a third effect appeared. The time constant for this effect, again, did not depend very much on the concentration.

Within a small concentration region, all three processes could be observed simultaneously as shown in Fig. 3.

At even higher concentrations, a fourth process was detected, which could be associated with the structural relaxation time and which also could be measured with oscillating rheology. All four processes are shown on Fig. 4.

While τ_2 has the opposite sign in comparison to τ_1, and τ_3 was only visible within a small concentration region of a factor 2, the other processes were visible over a large concentration region. Obviously, these results are very different than what is expected and much more information was in the electric birefringence results than in the rheological results. The data did not behave as expected from theoretical consideration, and has been explained as follows: τ_1 is the rotation of small rods in the electric field parallel to the field. τ_2 is explained by the alignment of small rods perpendicular to the electric field [17]. τ_3 is assumed to be due