Resonance growth of giant micelles in ternary surfactant solutions engendered by the addition of fatty acids

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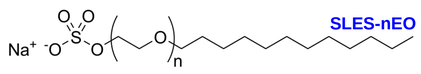
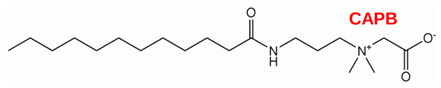
Goals of the study

- To investigate the effect of fatty acids on the formation of mixed micelles in ternary solutions.
- By polarized light microscopy, to check whether the investigated highly viscous samples are liquid-crystalline.
- Independently, by NMR to distinguish between liquid crystalline phase and dense isotropic micellar solution.
- Using Cryo-TEM, to determine the shape and size of the micelles.
- To check our hypothesis that discs should transform into either worm-like or ribbon-like micelles in the vicinity of the peak in viscosity.

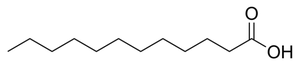
Materials



SLES-1EO = sodium lauryl-ethersulfate (SLES) with one ethylene-oxide group (anionic)



CAPB = cocamidopropyl betaine (zwitterionic)



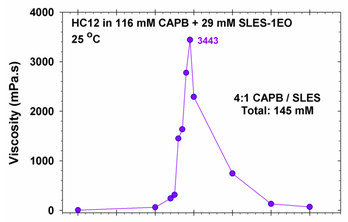
HL = lauric acid (fatty acid)

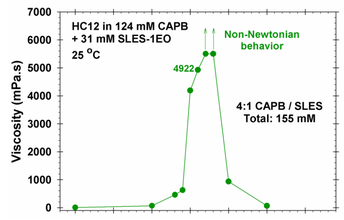
For brevity: 80 mM CAPB + 20 mM SLES = SS (Surfactant Solution)

Application in personal-care detergency: shampoos, shaving foams, etc.

Motivation: Formulations with Less Surfactant

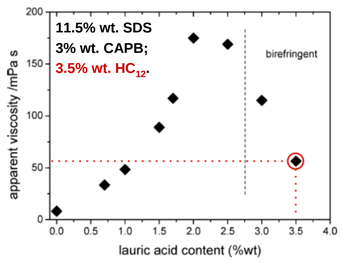
The fact that a relatively small additive of fatty acid causes the formation of very viscous surfactant solutions (of consistence like that of dense honey) can be used for creation of shampoo-type formulations.

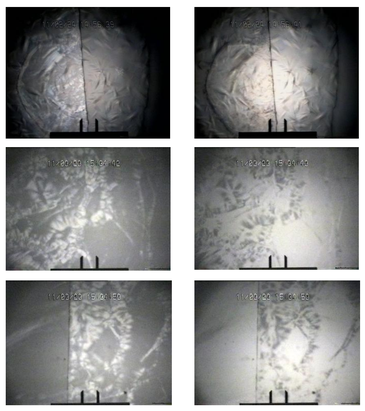




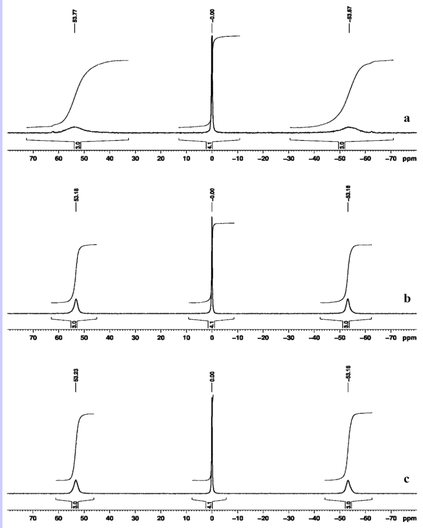
Liquid Crystals by Crossed Polarizers: Control Experiment

Experimental conditions at which liquid crystals are observed in the paper: [1] Colafemmina, G.; Recchia, R.; Ferrante, A.; Amin, S.; Palazzo, G. *J. Phys. Chem. B* 2010, *114*, 7250-7260.





Patterns (textures) that are typical for liquid crystals are observed. Left column – 0°; Right – 90° between the two polarizers.



Liquid Crystals by NMR: Control Experiments

^{23}Na NMR spectra of the test system [1] (11.5% wt. SDS, 3% wt. CAPB and 3.5% wt. HC12 in H_2O) obtained at a magic angle and the following conditions:

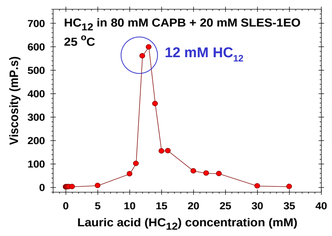
(a) Immediately after insertion of the rotor in the magnet;

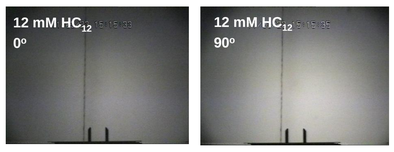
(b) After 24 hours during which the rotor was kept parallel to the magnetic field B_0;

(c) After 24 hours during which the rotor was kept perpendicular to the magnetic field B_0.

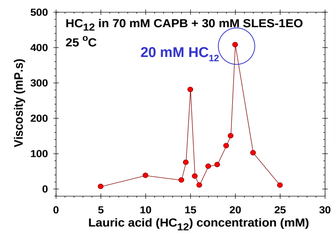
The presence of quadrupolar splitting independent of the orientation of rotor indicates the existence of liquid crystals in [1].

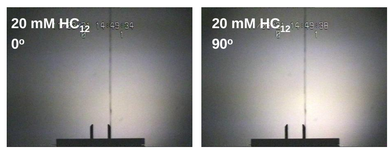
Liquid Crystals by Crossed Polarizers: Experiment for Our System





No indications for liquid crystal phases!





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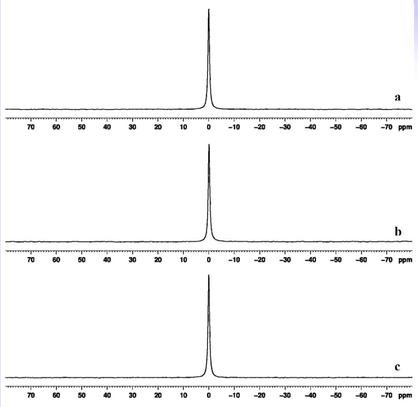


Liquid Crystals by NMR: Results for Our System

^{23}Na NMR spectra of our system (80 mM CAPB, 20 mM SLES and 11 mM Decanoic acid in H_2O) acquired at a magic angle and the following conditions:

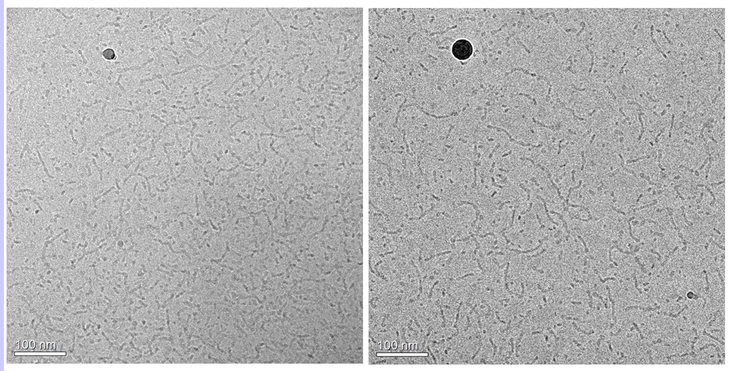
(a) Immediately after insertion of the rotor in the magnet;

(b) After 24 hours during which the rotor was kept parallel to the magnetic field B_0;

(c) After 24 hours during which the rotor was kept perpendicular to the magnetic field B_0.

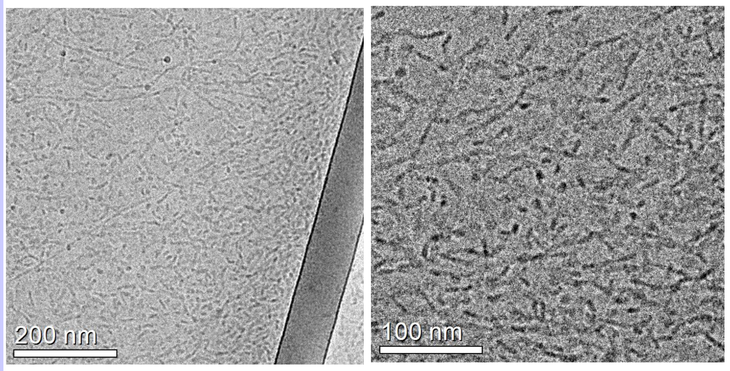
The ^{23}Na NMR spectra of our system show only one signal regardless of the orientation of the rotor and the time spent in the magnet. Hence, our system is an isotropic micellar solution rather than a solution containing liquid crystal phases (in agreement with the polarized-light experiments).

Cryo-TEM: SS (ca. 1.7 mPa.s)



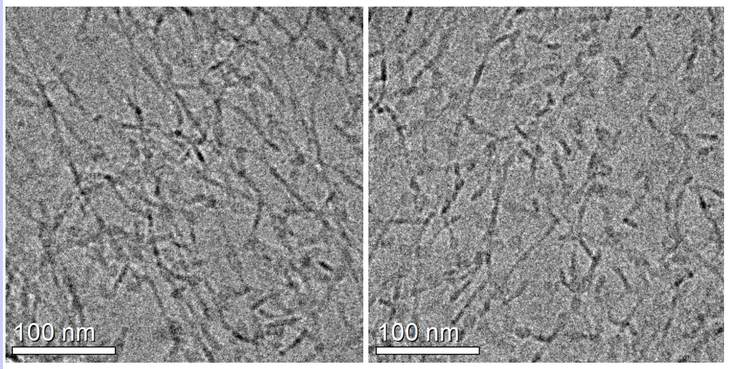
Spherical and rod-like micelles coexist in the base system (SS). Most elongated micelles have dumbbell-like shape – rods with swollen end caps.

Cryo-TEM: SS + 13 mM HL (ca. 112 mPa.s)



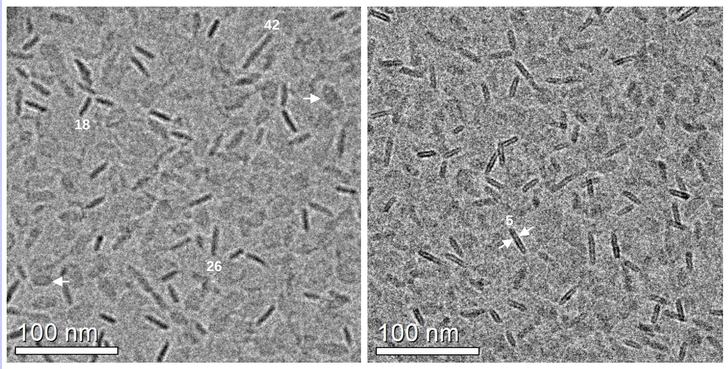
HL promotes micellar growth. Short rods transform to long worm-like micelles. The aspect ratio of the micelles increase abruptly compared to SS.

Cryo-TEM: SS + 20 mM HL (ca. 120 mPa.s)



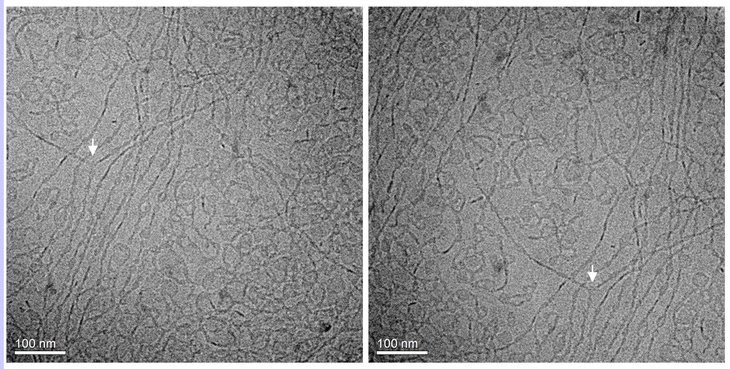
Long worm-like micelles with high aspect ratio. The thickness of the micelles undulates: there are small blobs superimposed on the worm-like structure. Probably due to component segregation along the micelle.

Cryo-TEM: SS + 25 mM HL (ca. 81 mPa.s)



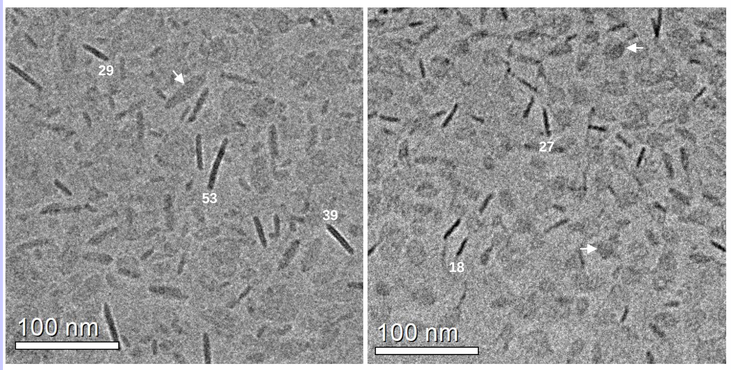
Worms transform to discs. The viscosity drops, because the aspect ratio decreases. The two layers in the discoidal part can be distinguished (right).

Cryo-TEM: SS + 30 mM HL (ca. 48 mPa.s)



The micelles become elongated again and branched. Formation of a micellar network: triple junctions (T-junctions) and loops. Branching (due to local inhomogeneity) leads to reduction of solution's viscosity.

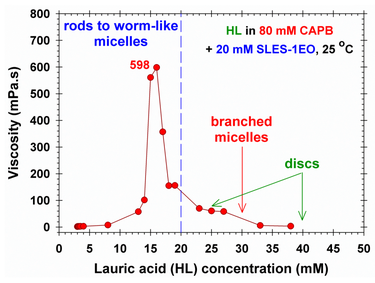
Cryo-TEM: SS + 40 mM HL (ca. 46 mPa.s)



Discs are the dominant form of self-assembly. Supposedly, at higher HL concentration, vesicles would form.

Summary and Conclusions

- Experiments with polarized light and NMR revealed that these viscous solutions are isotropic, i.e. we are dealing with micellar solutions, rather than with liquid-crystalline phases.
- HL promotes micellar growth. Short rods transform to long worm-like micelles. The aspect ratio of the micelles increase abruptly, followed by an increase in solutions' viscosity.
- After the peak in viscosity, worms transform to either discs or branched micelles.



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