Experimental report

15/02/2021

Proposal: **9-10-1610** **Council:** 4/2019

Title: Structural effects of flow on elongated alkylglycoside micelles

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Hexadecylmaltoside

Instrument	Requested days	Allocated days	From	To
D22	3	3	17/01/2020	20/01/2020

Abstract:

Alkylglycosides are non-ionic surfactants that are synthesised from renewable resources. They are used in several products, but their physico-chemical properties are not very well understood. Preliminary scattering experiments have shown that hexadecylmaltoside (C16G2) self-assembles into long rigid cylindrical micelles. Rheological experiments revealed that C16G2 samples are viscoelastic and shear thinning. These properties make C16G2 an interesting candidate to replace fossil-based surfactants currently used to obtain specific rheological properties of formulated products. With this proposal we want to determine how the structure and orientation of the micelles are affected by different shear rates to learn more about the alkylglycoside self-assembly.

Introduction

The behaviour of alkylglycosides is of interest due to their potential application in sustainable technologies as surfactants that can be synthesised from renewable resources.[1] We have recently reported the self-assembly of long tail sugar-based surfactants into a variety of micellar structures as defined by the monomer structure and the temperature of the system.[2,3] In particular, the anomeric configuration in the surfactant headgroup was proved to control micelle structure, leading to profound changes in the nanostructure of the system and hence in macroscopic rheology. As such, the formation of worm-like micelles by β-$C_{16}G_2$ leads to a shear-thinning, viscoelastic behaviour, whilst α-$C_{16}G_2$ globular micelles do not affect the rheology of the system and this remains Newtonian.

Experiment

The experiment performed on D22 (ILL) was focused on the study of the mechanism by which the nanostructure of the $C_{16}G_2$ micelles controls the macroscopic response of the fluid. For this purpose, 1-3 plane SANS measurements, using a Couette cell geometry, probed the structural changes in the micellar phase under shear. As such, we varied the following parameters in our samples and study them at different shear rates in the rheo-SANS setup:

1. Anomeric configuration of the surfactant – α-$C_{16}G_2$ and β-$C_{16}G_2$.
2. Surfactant concentration – 50, 100 and 200 mM for either α-$C_{16}G_2$ and β-$C_{16}G_2$.
3. Surfactant mixtures at different α-$C_{16}G_2$/β-$C_{16}G_2$ ratios and 100 mM total surfactant concertation.
4. Effect of temperature – 30 and 50 ˚C for 100 mM samples.

The system was characterised at shear rates between 0.01 s^{-1} and 1000 s^{-1}.

Results

Figure 1 shows the SANS data of β-$C_{16}G_2$ at different shears integrated in the q_x and q_y projections. It is clear that, upon shearing, the structure of the micelle network changes. As this anisotropy in the scattering is expected to arise from micelle alignment and breakage, we calculated the alignment factor of the α-$C_{16}G_2$ and β-$C_{16}G_2$ micelles upon shear from the anisotropy of the scattering. The scattered intensity as a function of the azimuthal angle is shown in Figure 2a and 2b for α-$C_{16}G_2$ and β-$C_{16}G_2$, respectively. Figure 2c shows the variation in the scattering intensity at two angles for the different shears. In addition, we have measured the scattering from high concentrations of surfactant (25, 50, 100 and 200 mM) in a wider q-range in order to determine micelle structure at zero-shear.

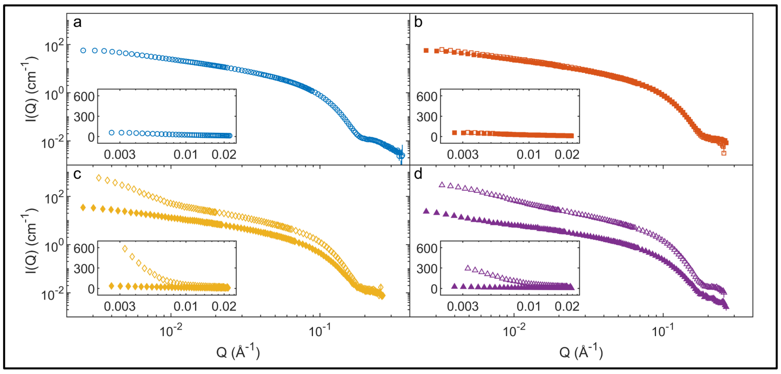

Figure 1 Average intensity from the vertical (unfilled) and horizontal (filled) sectors for 100 mM β-$C_{16}G_2$ at 50 °C. Results shown for shear rates of 0 (blue ○), 10 (red □), 100 (yellow ◊) and 1000 (purple △) s^{-1}.

The results from the rheo-SANS showed that upon shear, the entangled network of WLM formed by β-$C_{16}G_2$ begins to align, whilst the shorter rod-like aggregates of α-$C_{16}G_2$ do not show significant alignment. This is connected to the rheology of each system, as the longer micelles result in non-Newtonian behaviour and the shorter aggregates do not modify the rheology of the system. Segmental alignment correlates with the reduction of viscosity in connection to micelle morphology in the surfactant mixtures. A decrease in alignment is observed for decreasing ratio of β-$C_{16}G_2$, which connects to the formation of shorter micelles as seen in the dilute regime.

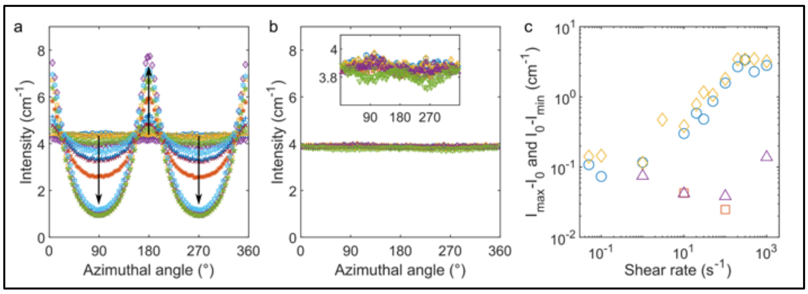

Figure 2 Intensity as a function of azimuthal angle for 100 mM β-$C_{16}G_2$ at 50 °C (a) and 100 mM α-$C_{16}G_2$ at 50 °C (b) for q=0.05 ± 0.005 Å and shear rates from 0 to 1000 s^{-1}. The evolution of the data upon increasing shear follows the direction marked with the black arrows. c) Difference in intensity for different shear rates and at no shear at 180° (β (○) and α (□)) and 90° (β (◊) and α (△)).

Variations in concentration and temperature also showed an effect in the resulting rheology that is connected to the micelle structure. At the higher surfactant concentration, the alignment is more pronounced in comparison to the lower concentrated sample. This was attributed to two effects, the formation of longer micelles and a more entangled network at higher surfactant concentration. Temperature induces a similar variation in micelle alignment. Higher temperatures, which have been shown to result in longer micelles, experience earlier and more pronounce alignment upon shear.

Previous rheological characterisation of the system showed that micelle breakage was the dominant relaxation mode upon shear. Based on this rheo-SANS results, the observed alignment arises from the orientation of micelle segments in the direction of the flow. In addition, longer micelles might result in longer segments upon breakage. As longer segments align faster due to their slower rotational diffusion, more pronounced alignment is observed for the systems with neat or higher ratio of β-$C_{16}G_2$. As such, the mechanism of the rheological modification induced by the self-assembly of α- and β-$C_{16}G_2$ is shown to be connected to the nanoscale structure of the micelles. These results provide a detailed understanding on the function-structure relationship of the sugar-based self-assemblies, assisting the development of new technologies, such as response materials and drag-reducing agents, based on these sustainable surfactants.

Conclusion

The outcome of this experiment has been highly positive with a major contribution from our local contact, Lionel Porcar. Furthermore, the data obtained is high quality with a good signal-to-noise ratio, and the instrument and sample environment functioned well during the experimental time.

This study is an important part of the systematic investigation of the behaviour of sugar-based surfactants. Also, the investigations performed on D22 were part of the PhD project of Dr. Johan Larsson, who successfully defended his thesis in January 2021. A manuscript is in the final steps of preparation and will soon be submitted for publication. Furthermore, this investigation also provides a valuable point of view to the industrial partners of the project, who have witnessed the possibilities of SANS characterisation of complex systems.

This project will continue with future investigations on the self-assembly of oligomeric sugar-based surfactants and how the number of sugar units of the headgroup allows tunning the properties of the system.

References

[1] Holmberg, K., *Natural surfactants.* Current Opinion in Colloid & Interface Science, 2001. **6**(2): p. 148-159.
[2] J. Larsson et al., *Effect of the Anomeric Configuration on the Micellization of Hexadecylmaltoside Surfactants*, Langmuir 35(43) (2019) 13904- 13914.
[3] J. Larsson et al., *Molecular structure of maltoside surfactants controls micelle formation and rheological behavior*, J. Colloid Interface Sci. 581(Pt B) (2021) 895-904.