Experimental report

16/09/2019

Proposal:	**9-10-1586**	**Council:**	10/2018
Title:	Molecular self-assembly in hydrogen-bonding rich non-aqueous solvents		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**WUGE H BRISCOE**
Experimental team:	Lauren MATTHEWS WUGE H BRISCOE Michael STEVENS Bhaveshkumar BHARATIYA
Local contacts:	Ralf SCHWEINS

Samples:	SDS C16TAB DDAB d-glycerol DTAB Ethylene Glycol

Instrument	Requested days	Allocated days	From	To
D11	3	3	30/08/2019	02/09/2019

Abstract:

Hydrogen-bonding is a key fundamental parameter in self-assembly of amphiphiles, driving aggregation via the hydrophobic effect. Hydrogen-bonding rich non-aqueous solvents are of interest as they are analogous to water, the archetypal solvent with a dense hydrogen bonded network. Non-aqueous solvents can provide advantages, such as high boiling points and excellent solvency for organic molecules. However, self-assembly in H-bonding rich non-aqueous solvents is not well understood. Here, in collaboration with the GSK Oral Health Division, we propose a small-angle neutron scattering study (SANS) of self-assembled structures formed by surfactants in several H-bonding rich non-aqueous solvents, including ethylene glycol, propane-1,3-diol and propylene glycol, which vary in the H-bonding number and density. We will vary surfactant architecture (comparing anionic, cationic and zwitterionic surfactants), as well as the surfactant concentration. We also propose to investigate the temperature effect on these systems, as it has been shown in preliminary studies to have a profound effect on the self-assembly mechanism.

Experiment Objectives

Hydrogen-bonding is a key fundamental parameter in self-assembly of amphiphiles, driving aggregation via the hydrophobic effect. Hydrogen-bonding rich non-aqueous solvents are of interest as they are analogous to water, the archetypal solvent with a dense hydrogen bonded network. Non-aqueous solvents can provide advantages, such as high boiling points and excellent solvency for organic molecules. However, self-assembly in H-bonding rich non-aqueous solvents is not well understood. Here, in collaboration with the GSK Oral Health Division, we propose a small-angle neutron scattering study (SANS) of self-assembled structures formed by surfactants in several H-bonding rich non-aqueous solvents, including ethylene glycol, propane-1,3-diol and propylene glycol, which vary in the H-bonding number and density. We will vary surfactant architecture (comparing anionic, cationic and zwitterionic surfactants), as well as the surfactant concentration. We also propose to investigate the temperature effect on these systems, as it has been shown in preliminary studies to have a profound effect on the self-assembly mechanism.

Experiment Report

During our time at D11, measurements were taken to characterise the bulk structure of surfactants and lipids in non-aqueous solvents, for example: ethylene glycol, and glycerol. These measurements were carried out at different temperatures as temperature was found to have a profound effect, structurally, on these types of materials. The results from this experiment will be used in combination with those from ISIS LOQ and SANS2D (RB: 1810629 and 1910080 respectively) to look at the fundamental mechanism of self-assembly in hydrogen-bonding rich non-aqueous solvents.

Initial analysis of the data obtained in this experiment involved plotting the raw intensity against Q to study the evolution of the structure with temperature and surfactant concentration. Figure 1 is an example of data obtained using DTAB and glycerol, where the structural transition between a gel-like material and a liquid-like material can be seen. The transition is also shown to be reversible, upon cooling to 25 C the mesophase structure returns.

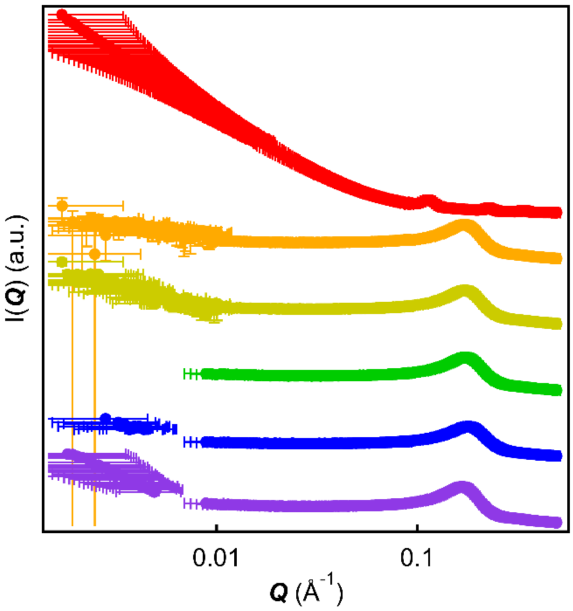

Figure 1 Raw SANS data of 1000 mM DTAB in glycerol, shown at various temperatures, 25 °C (**red**), 40 °C (**orange**), 45 °C (**yellow**), 50 °C (**green**), 70 °C (**blue**), 25 °C (after cooling, **purple**).

Further study was carried out on the SDS in glycerol gels, by the addition of various salts to the gel-like phase, but initially a control sample of SDS in glycerol without gel was measured (**Figure 2**). The resulting scattering pattern shows the same results as seen in previous scattering experiments at other beamlines, where the presence of a large mesophase with lamellar Bragg peaks is seen at room temperature and becomes micellar upon heating.

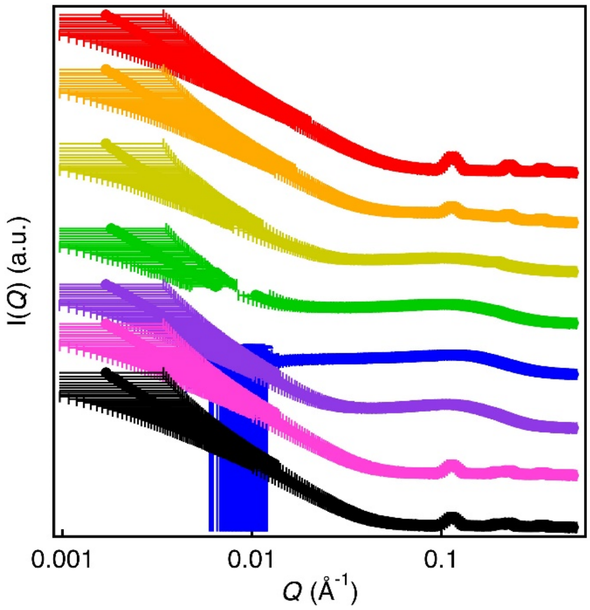

Figure 2 Raw SANS data of 220 mM SDS in glycerol, shown at various temperatures, 25 °C (**red**), 40 °C (**orange**), 45 °C (**yellow**), 50 °C (**green**), 70 °C (**blue**), 25 °C (after cooling, **purple**), 25 °C (after cooling 2 hrs, **pink**), 25 °C (after cooling 4 hrs, **black**).

Figure 3 shows the addition of salts at just 0.1 wt %, where the effects on the structure upon cooling is quite striking. The change in morphology upon cooling is apparent, where the none of the three curves on the right can be overlaid onto the control. Sodium fluoride seemingly removes structure from the system, hence the appearance of only two Bragg peaks, whereas magnesium fluoride seems to have a mixed lamellar phase, resulting in four Bragg peaks.

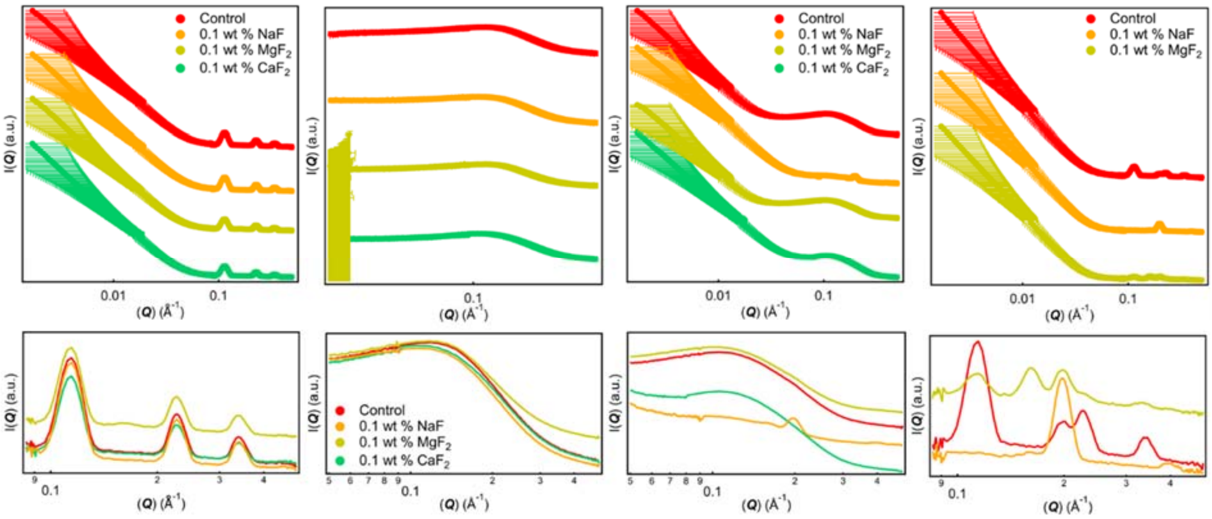

Figure 3 Raw SANS data of SDS in glycerol with 0.1 wt % added salts, shown by the legend. (**Top**) Full SANS dataset, (**Bottom**) zoomed in to observe the mesophase peaks. From **left** to **right**: 25 °C before heating, 70 °C, 25 °C after cooling, 25 °C after cooling for 4 hrs.

Finally, **Figure 4** shows the effect of increasing sodium fluoride concentration on the system, from 0.1 wt % to 10.0 wt % sodium fluoride. Here shown, there is no effect from initial preparation, where the mesophase peaks in all four samples overlay the control without salt. In the 70 °C data, an effect can be seen, where the shift in *Q* shows that the size of the micellar aggregates is changing with addition of salt. Lastly, a striking morphological change can be seen upon cooling the micellar phase back to the gel-like phase.

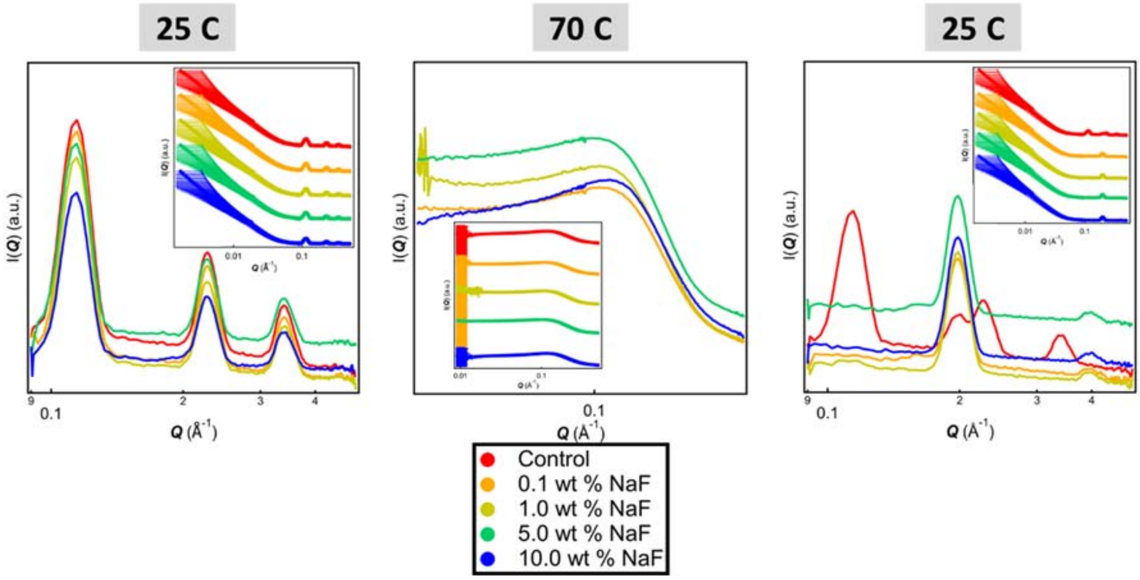

Figure 4 Raw SANS data of SDS in glycerol with increasing sodium fluoride content, indicated by the legend. Datasets are shown enlarged to highlight the mesophase peaks, however, full datasets can be seen in the insets.