Experimental report

10/02/2022

Proposal: **9-10-1716**

Council: 4/2021

Title: Advanced lubricants for CO2 emission reduction: effects of shear on reverse cylindrical/wormlike micelles

Research area: Chemistry

This proposal is a resubmission of 9-10-1607

Main proposer: **Julian EASTOE**

Experimental team: Florence GROS
Ilona SERAFIN
ADHIP RAHMAN
Georgina MOODY

Local contacts: Sylvain PREVOST

Samples: alkanes-surfactants-water
DDAB (C26H56BrN)
NaAOT (C20H37NaO7S)
Mg(AOT)2 (C40H74MgO14S2)
Ni(AOT)2 (C40H74NiO14S2)
d-cyclohexane (C6D12)

Instrument	Requested days	Allocated days	From	To
D11	2	0		
D33	2	2	09/10/2021	11/10/2021
D22	0	0		

Abstract:

To determine the effect of shear on micellar alignment and interactions, Rheo-SANS will be used to study reversed cylindrical micelles in d-cyclohexane. Different types of surfactant (Figure 1) will be studied, but at (approx.) the same micellar dimensions. These systems have been previously characterized under equilibrium conditions on Larmor and D11 (RB1920023 and 9-10-1607). This new proposal represents the next step, to investigate shear effects. The results will guide formulation of super-efficient lubricant additives for reducing friction, improving wear, and reducing CO2 emissions from internal combustion engines (ICEs). The work is part of a 3.5 year PhD program (G. Moody) fully funded by Infineum. This is a resubmission of 9-10-1688 addressing the panel comments.

9-10-1716

Title: Advanced lubricants for CO2 emission reduction: effects of shear on reverse cylindrical/wormlike micelles
Investigators: Georgina Moody, Ilona Serafin, Adhip Rahman, Prof. Julian Eastoe
Instrument: D33
Beamline contact: Sylvain Prévost
Dates: 09/10/2021 – 11/10/2021 (2 days)

Note: Due to scheduling issues because of COVID-19, this experiment was changed from a rheo-SANS to an automatic sample changer study.

Car engine oil lubricants are specifically formulated with a variety of additives that maximise mechanical efficiency. One such variety are friction modifiers that consist of polymers and surfactants. Reverse micellar systems in this oily media are known to aid with lubrication properties which poses the question as to whether the shape of the micelle gives an added advantage to reducing friction i.e., spheres vs cylinders. This experiment aims to build upon the systems that were investigated on the instrument Larmor at ISIS Neutron & Muon Source (RB1920023) in Nov 2019, and D11 at the ILL (9-10-1607) in Feb 2020. The aim of this investigation was to monitor the effect of temperature upon surfactants of varying concentrations, water content (w = [H_2O]/[surfactant]), with or without the addition of a hydrotrope (a primitive amphiphilic species) where x = 0 – 0.3 (x = [Hydrotrope]/[Surfactant]), and the effect of an increasing hydrotrope alkyl chain length (from C_2 – C_8).

Table 1 outlines the structures of the surfactants and hydrotropes that were used. Two concentrations were used (50mM, 100mM), two w values (5 and 10), and an x value of 0.1 was used for all hydrotropes apart from Na-C_2, which had an added investigation of increasing x value from 0.1 – 0.3. Temperatures set to be investigated were 25, 35, 45, and 55°C. Unfortunately, there was an issue with the scripts written for the water baths which meant data collecting at 35°C was often missed. There was also a mechanical problem with the moving stage of the experiment that has meant some scattering profiles are missing due to the sample being offset from the beam.

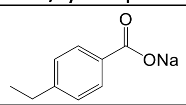
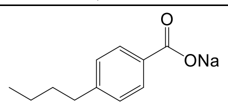
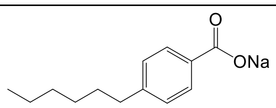
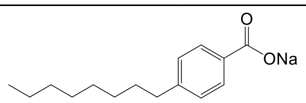
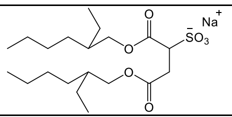
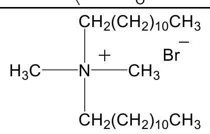
Surfactant/hydrotrope structure	Name
	Sodium 4-ethylbenzoate (Na-C_2)
	Sodium 4-butylbenzoate (Na-C_4)
	Sodium 4-hexylbenzoate (Na-C_6)
	Sodium 4-octylbenzoate (Na-C_8)
	Sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT)
	Didodecyldimethylammonium bromide (DDAB)

Table 1: Structures and names of surfactants and hydrotropes used in this experiment

So far, the SANS profile intensities have been divided by 2 and primitively plotted to check for any obvious trends and outlier profiles. There were a few phase separations that may have occurred while in the beam –

as can be seen by some large differences in intensities between the scattering profiles, but a vast majority have remained stable. First impressions of the data give the following indications:

- Increasing temperature shortens cylindrical micelles more towards structures that look spherical-like i.e. sample GM184 → 50mM DDAB w = 5 x = 0 (see **Figure 1**)
- Spherical micelles appear to get smaller as temperature is increased i.e., sample GM270 → 100mM NaAOT w = 10 x = 0 (see **Figure 2**).
- The addition of hydrotrope into the system seemed to amplify the effect temperature has on micellar shrinkage for anionic surfactant NaAOT systems. Comparing **Figure 4** and **Figure 5**, this system consisted of 100mM NaAOT w = 10 x = 0 to 0.1 of NaC_2 hydrotrope, there seems to be a big difference in the scattering intensities of profiles ranging from 25 to 55°C. It is still too early to say whether this is the case though as other system scattering profiles do not show this too obviously.
- The opposite of the above point may be made about DDAB. Although increasing temperature shortens the cylindrical micelles, it seems to be at a lesser degree once a hydrotrope is added in vs without.
- Using a longer hydrotrope alkyl length appears to be more efficient at shortening DDAB cylindrical micelles than using a greater amount of a shorter hydrotrope. Comparing **Figure 2** with **Figure 3**, the depression of the 25°C curve appears to be greater when x = 0.1 of NaC_8 is used vs x = 0.3 NaC_2 within a 50mM DDAB w = 5 system.

Data fitting is currently underway, it will be interesting to see if the addition of an increasing amount of hydrotrope, or if the addition of a hydrotrope with an increasing alkyl chain will increase or lessen the impact temperature has on the micellar shortening/shrinking. The results from this experiment will form part of a PhD thesis and will be communicated with industrial sponsors Infineum UK Ltd in the hopes to gain an initial understanding on the effects of temperature on micellar systems and how they may behave once under internal combustion engine conditions. An updated version of this report will be uploaded once data fitting has been completed. The figures below are only a selection of SANS profiles.

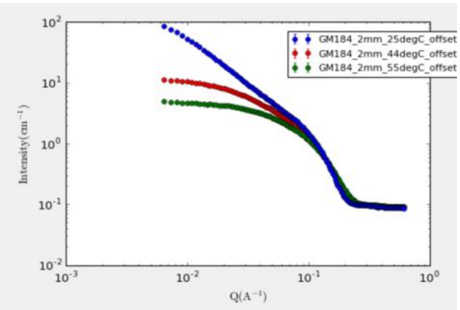


Figure 1: 50mM DDAB w = 5 x = 0

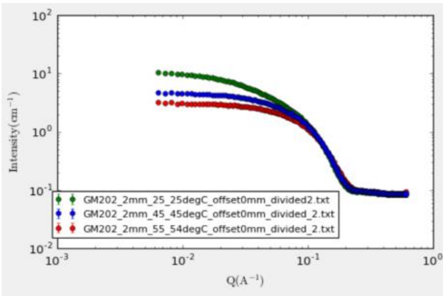


Figure 2: GM202: 0.05M DDAB w = 5 x = 0.1 NaC_8

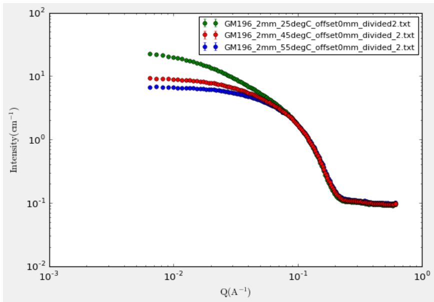


Figure 3: 0.05M DDAB w = 5 x = 0.1 NaC_2

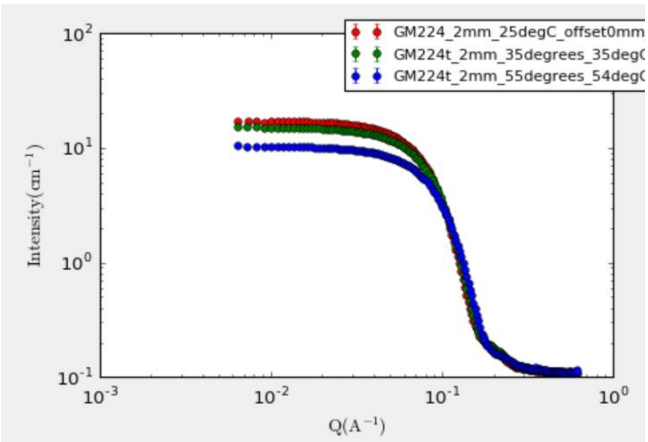


Figure 4: 100mM NaAOT w = 10 x = 0

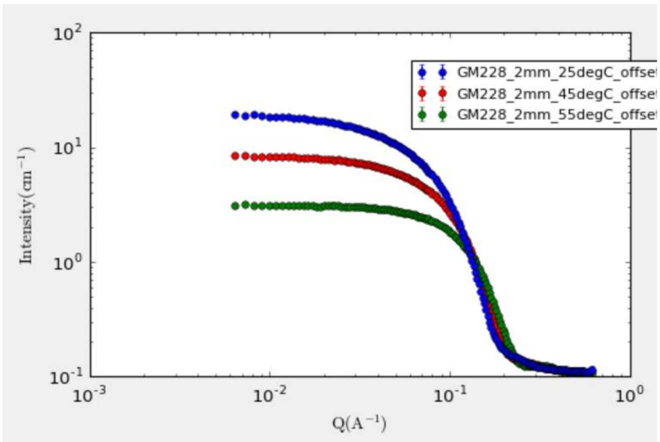


Figure 5: 100mM NaAOT w = 10 x = 0.1 NaC_2