Experimental report

08/02/2021

Proposal: 9-10-1607 **Council:** 4/2019

Title: New lubricant additives based on cylindrical reversed micelles

Research area: Chemistry

This proposal is a new proposal

Main proposer: Julian EASTOE

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Samples: water-surfactants-hydrotropes-cyclohexane

Instrument	Requested days	Allocated days	From	To
D11	2	2	10/02/2020	12/02/2020
D22	2	0		
D33	2	0		

Abstract:

Contrast variation SANS will be used to study structures of reversed micelles in cyclohexane, and in particular to reveal effects of hydrotrope addition for promotion and growth of cylindrical micellar aggregates. This equilibrium study represents the first stage of a broader project, which will involve future high pressure/temperature and shear experiments, aimed at understanding the recently discovered role of reversed micelles as lubricants1. The new results will allow to: a) identify and quantify the initial micellar structures, b) understand the formation of long flexible wormlike reverse micelles and c) help guide design of new highly efficient lubricants that have potential to improve friction and wear and to reduce CO2 emissions from combustion engines. This is the first stage in a new 3.5-year PhD program to develop optimized lubricant oils, and Georgina Moody is a 1st year PhD student, fully funded by the lubricant additive company Infineum.

9-10-1607

Title: New lubricant additives based on cylindrical reversed micelles

Instrument: D11

Dates: 10/02/2020 – 12/02/2020 (2 days)

UPDATED REPORT (08/02/2021)

Car engine lubricants are composed of a variety of additives, specially formulated to maximise mechanical power efficiency. Friction modifiers are a type of additive that consists of polymers and surfactants. As reverse micelles in oily media are known to aid with the lubrication of the oil, the question which has underpinned this investigation is whether the shape of the micelle impacts friction reduction (i.e. does having spherical or cylindrical/wormlike micelles make the difference). This experiment aimed to build upon the systems we had developed at ISIS Neutron & Muon Source in November 2019 on the instrument Larmor (**RB1920023**) to collate together a library of micellar systems with varying shapes and lengths which could be tuned through a variety of factors. These factors include changing the surfactant type i.e. using cationic/anionic/zwitterionic surfactants, changing the water content within the system (w = *[H_2O]/[surfactant]* = 5 or 10 gave micellar structural changes), or by adding in an additional amphiphilic species known as hydrotropes (x = *[Hydrotrope]/[Surfactant]* typically x = 0.1).

The experiment **RB1920023** built upon the effect of changing the x value of the same hydrotrope (Sodium 4-ethylbenzoate) from 0.1 – 0.3. However, this experiment on D11 focused upon the effect of altering the alkyl length of the hydrotropes used. **Table 1** outlines the structures of the hydrotropes, and surfactants used. Two concentrations were also studied (50mM and 100mM), as well as the two w values 5 and 10.

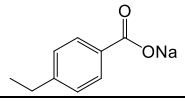
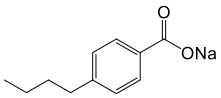
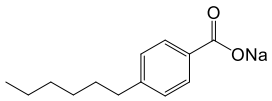
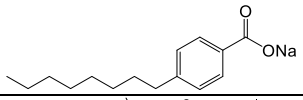
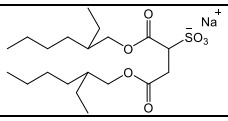
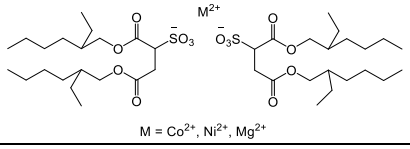
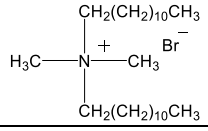
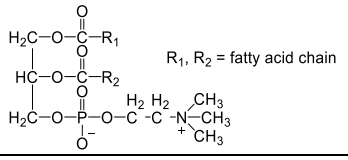
Surfactant/hydrotrope structure	Name
	Sodium 4-ethylbenzoate (Na-C2)
	Sodium 4-butylbenzoate (Na-C4)
	Sodium 4-hexylbenzoate (Na-C6)
	Sodium 4-octylbenzoate (Na-C8)
	NaAOT
 M = Co^{2+}, Ni^{2+}, Mg^{2+}	$M^{2+}(AOT)_2$ where M = Co, Ni, Mg. Divalent metal AOT surfactant
	Didodecyldimethylammonium bromide (DDAB)
 R_1, R_2 = fatty acid chain	Lecithin

Table 1: Surfactant structures and names used in this experiment.

Fitting of the SANS data is currently underway, a selection of example spectra are shown in **Table 2**. The main results gleaned from them so far is that:

- For the cases involving anionic surfactant ($M^{2+}(AOT)_2$) /anionic hydrotrope, there is an increase of cylindrical length from x = 0 to x = 0.1 no matter on what alkyl length the hydrotrope possesses (This is by comparing with results from **RB1920023**.)
- Cationic surfactant (DDAB)/anionic hydrotropes show a stepwise decrease in cylindrical length as hydrotrope alkyl length increases.
- There does not seem to be a clear trend when combining the zwitterionic surfactant lecithin with the anionic hydrotropes, although a more in-depth investigation is needed.
- Changing the w value from 5 to 10 increases the radius but decreases the cylindrical length.
- Although some SANS profiles do not show any obvious changes of cylindrical length as different hydrotropes are added, this may need to be fully confirmed through data fitting.

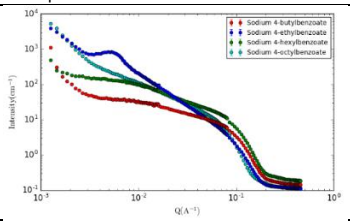
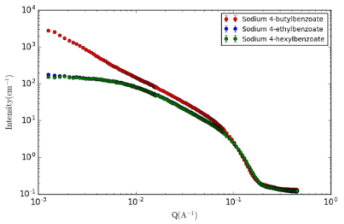
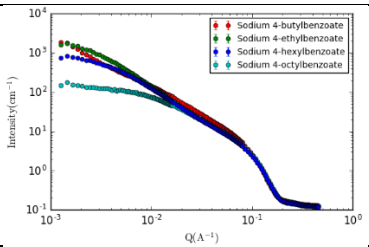
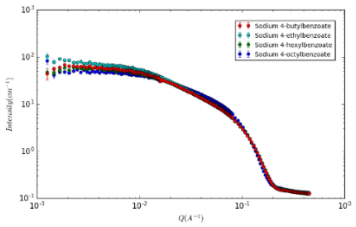
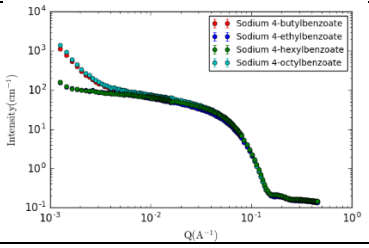
Surfactant	Concentration (mM)	*w* value	SANS profiles
$Mg(AOT)_2$	100	5	
$Co(AOT)_2$	100	5	
$Ni(AOT)_2$	100	5	
DDAB	100	5	
Lecithin	100	5	

Table 2: A selection of SANS profiles for a variety of surfactants, concentrations, and w values. Each SANS profile shows effect of adding in a hydrotrope of increasing alkyl length [all at x = 0.1].

In many cases, there may not be a clear trend relating hydrotrope alkyl length to cylindrical length, these results will add into the matrix of surfactant systems in which we can carefully select systems for further study. These results will be put towards a PhD thesis chapter, communicated back to my PhD sponsors Infineum UK Ltd as well as to Prof P. Camp (University of Edinburgh) for use in Molecular Dynamics modelling of micelles in lubricants. Future work involves possibly looking into the effect of using cationic hydrotropes instead of anionic hydrotropes to resolve the possible headgroup interactions occurring between the surfactants and hydrotropes. The library of systems we are generating can then allow for selectively choosing systems of various lengths and micellar types to study effects of shear (so as to attempt to answer the initial question above of micellar shape affecting friction reduction). This will be done through methods in lab (rheology, equipment provided by Infineum), and potentially with future neutron scattering (RheoSANS, and a custom tribometer build by Prof A. Routh and his group at the University of Cambridge).

UPDATE 08/02/2021:

Since submitting this report, extensive SANS data analysis has been carried out, combining the results from this experiment and the Larmor experiment (**RB1920023**). The combination has equated to approximately 130 SANS spectras. All of which have had Guinier, Porod, and SasView analysis carried out. Snapshots of this collated library of samples are shown at the end of this document. When fitting each sample in SasView, great care was taken to ensure that each SANS profile had the correct model fitted. To do this, various models were trial fitted before the end selection. This was carried out for each SANS spectra, but two examples have been selected to showcase this:

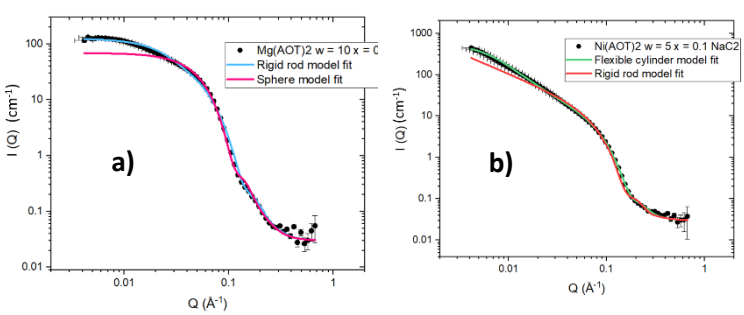


Figure 1: Examples of how the correct model was selected when analysing the SANS data. a) 100mM $Mg(AOT)_2$, w = 10, x = 0, R = 25 Å, L = 200 Å. b) 100mM $Ni(AOT)_2$, w = 5, x = 0.1 of sodium 4-ethylbenzoate (Na-C2)

As is shown by spectra **a)** and **b)**, the selection of model fit for the SANS profiles is important. E.g. **a)** $Mg(AOT)_2$ was initially attempted to be fitted with a spherical model before a rigid rod model was applied, which gave a much closer fit. Similarly **b)** $Ni(AOT)_2$ in this example was initially fitted with a rigid rod model before it became apparent that this system benefitted from the added parameter of Kuhn length that made up the flexible cylinder model.

Some of the trends that have come to light since fitting the data are:

- NaAOT saw a spherical → cylindrical micellar transition as the amount of hydrotrope added to the system was increased from 0 to 0.3
- DDAB saw a shortening of micellar length e.g. 288 Å to 155 Å (100mM DDAB, w = 5) when x was increased from 0.1 to 0.3. DDAB also saw that by increasing the alkyl length i.e. x = 0.1 of Na-C2 to Na-C8 for 100mM DDAB, w = 5, L decreased from 350 Å to 170 Å.
- $Mg(AOT)_2$ saw an increase in flexibility as hyrotrope was added in i.e. the rigid model shifted to flexible cylinders when going from x = 0 to 0.1. Increasing the hydrotrope alkyl length that was doped in did not seem to have an effect upon the micellar length.
- $Ni(AOT)_2$ and $Co(AOT)_2$ all existed as flexible cylinders as this model was the only model that would fit these. Increasing x i.e from 0 to 0.3 decreased the length of $Ni(AOT)_2$ i.e. for 100mM $Ni(AOT)_2$, w = 5, from 2500 Å to 1390 Å. Whereas for $Co(AOT)_2$ there was no affect upon the micellar lengths.