Experimental report

18/03/2019

Proposal: 9-10-1533

Council: 4/2017

Title: Automated sampling and spectroscopic resolution of structure and composition of hydrogenous and fluorinated surfactant mixed micelles

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Perfluorononanoic acid
Brij-35
pyrene

Instrument	Requested days	Allocated days	From	To
D22	2	1	23/04/2018	24/04/2018

Abstract:

Fluorocarbon surfactants are used for example in fire-fighting foams, paints, and as stain repellents. Attractive properties include their degradation resistance and surfactant properties with lower surface tension than C-H analogues. However, due to their stability they accumulate in the environment, can leach to the groundwater and contaminate drinking water reservoirs or can be taken up by plants and soil organisms.

The present proposal extends studies on a model mixed system of hydrogenous and fluorinated surfactants, for which there is already background information but little detailed structural information. The large number of samples required for the analysis of mixtures emphasises the need for automated sample delivery. We wish to demonstrate the usefulness of a flow-through cell with automatic sample mixing using an HPLC pump, and additional information to constrain the model from in-line marker dye fluorescence and density measurements. Understanding fluorocarbon surfactant structural behaviour and partitioning of fluorescent marker dyes (pyrene) will allow optimisation of their use as well as diminution of adverse effects both for health and in the environment.

Report on Experiment 9-10-1533 on D22, from 23/04/2018 to 24/04/2018

Automated sampling and spectroscopic resolution of structure and composition of hydrogenous and fluorinated surfactant mixed micelles

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We have carried out the experiment 9-10-1533 (D22) with the aim to establish a new multimodal characterization method that includes: UV-Vis absorption, fluorescence emission, density measurement and neutron small angle scattering (i.e. NUrF).

The work presented first some technical challenges; and, second some scientific questions.

1. Technical challenges and achievements

The technical challenges and achievements are summarized in the table below:

Technical objectives	**Achievements**
1. *Fit the UV-visible spectroscopy on flow cell*	Done
2. Fit the Fluorescence emission on flow cell	Not possible, no ports were usable for fluorescence
2. *Software control*	
2.1. Driver for spectrometers	Done
2.2. Driver for Densitometer	Done
2.3. Driver for monochromator (fluorescence excitation light)	Done
2.4. Driver for pumps (standard Knauer pumps)	Done
2.5. Shutter controls for UV and FL lamps	Done
3. *Nomad integration*	
3.1. Time stamping	Done
3.2. Nexus data file structure	Done
3.3. Data visualization	Not ready
3.4. Automation of experiments	Done
What next?	
1. A dedicated flow cell holder to allow for fitting of spectroscopy probes	
2. Improved data retrieval for “online” analysis	

Figure 1 shows the setup offline and online at D22. Note that the densitometer was used in-line after the flow cell.

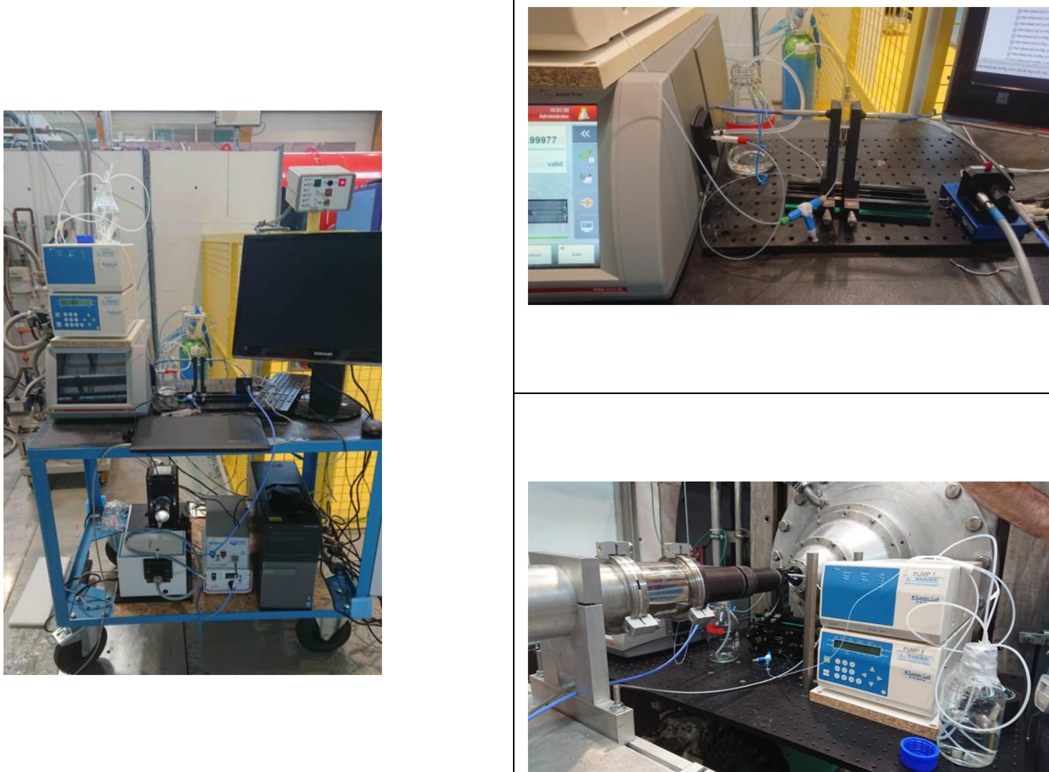

Figure 1. Offline NURF at D22 (April 2018). Left panel top of table: Densitometer (Anton Paar), pumps (Knauer) and flow cell in holder with fiber optics. Lower tableshelf: UV and fluorescence light sources and spectrometer. Right panel (top), zoomed in image of flow cell with side fiber optics attachment and sample tubing. Right panel (bottom), at the beamline.

2. Scientific objectives and outcomes

The chosen scientific case aimed at verifying and determining how Brij35/PFNA surfactants system behave with and without a reporting fluorescent dye (pyrene). The table below summarises the scientific objectives and achievements:

Scientific objectives	Achievements
1. Brij35/PFNA/Pyrene - 1mM (and 5mM) surfactants mixture in D_2O with or without in 1uM pyrene - Contrast match at 65% D_2O	
1.1. Automated mixing of surfactants with and without pyrene.	Done: Typically, 11 samples (volume fraction Brij35: PFNA / 0, 10, 20, 30 40, 50, 60, 70, 80, 90, 100) automatically mixed and flow through using the pump.
1.2. Enhanced data: SANS, UV, FL and Density	Partial – Fluorescence was not possible due to the geometry of the available flow cell. Only UV and SANS was recorded.

Results for a typical mixture of Brij35-PFNA

We could only measure the surfactants at both 1mM concentration. The low concentration resulted in weak SANS data. Typically the SANS were collected for 480s and the associated transmission for 60s. In total a full run of 11 samples at the various volume fractions took a bit less than 2 hours. The integrated automation in Nomad was a success a proof that with the added information from the spectroscopy and density, this type of experiment can yield new insights into a 2 components system. Interestingly, the addition of a densitometer allowed to accurately determine the composition of the mixtures!

Practically, a volume of about 1.3mL was needed to fill the system for each mixture composition. The volume can be further reduced.

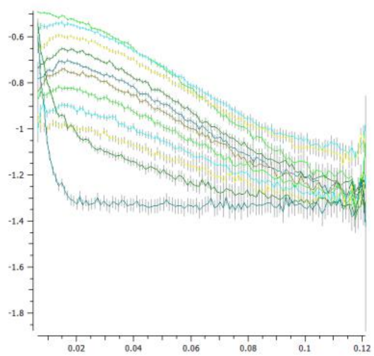

Figure 2. Brij35-PFNA 1mM in D20 from 100:0 to 1:100 vol:vol in steps of 10.

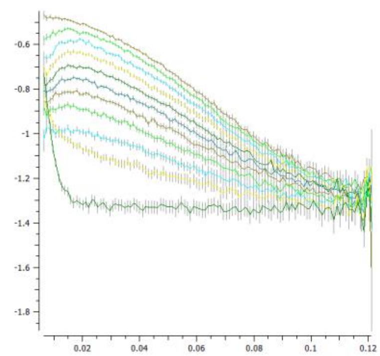

Figure 2. Brij35-PFNA 1mM in D20 from 100:0 to 1:100 vol:vol in steps of 10. In the presence of 50uM of pyrene.

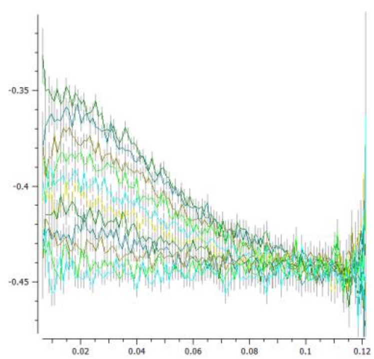

Figure 4. Contrast match condition for Brij35 (65% D2O – 35% H2O) and titration with increasing volume ratio of PFNA (similar to figure 3) in the presence of 50uM pyrene.

The results highlighted a few shortcomings of the experimental idea: (i) 1mM is too close of the Brij35 cmc, yielding poor scattering intensities; (ii) the lack of fluorescence probe precluded any evaluation of the pyrene behaviour. No useful information could be extracted from the UV spectra.

In conclusion, we demonstrated that the automation of the pump mixing, in line density and UV spectroscopy could yield robust experimental design and higher throughput experiments. From this we anticipate the design of a new flow cell holder and further integration into Nomad.