Experimental report

30/03/2017

Proposal:	**INTER-354**	**Council:**	10/2016
Title:	Internal time on D11		
Research area:			

This proposal is a new proposal

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Samples: aqueous surfactant solutions with small amounts of HCI and NaOH

Instrument	Requested days	Allocated days	From	To
D11	1	1	20/01/2017	21/01/2017

Abstract:

Abstract

The purpose of this experiment was twofold: firstly to test and characterise a continuous-flow chemical reactor sample environment and secondly to study the morphological evolution of a commercial surfactant with pH. The development of new sample environments is being conducted as part of a BMBF project at the Technical University of Berlin and the ILL, intended to expand the range of soft-matter research that can be accomplished at SANS beamlines. A commercial aqueous surfactant system was chosen as it is relatively well known[1-3], non-toxic and air-stable. Preliminary small-angle scattering experiments had shown that the structure of the micellar aggregates formed in aqueous solution depends on the pH of the system; at low pH, bilayer or vesicle structures are formed whereas at high pH, small spherical micelles are favoured. Structural changes in micellar architectures can have important consequences on the rheological and optical properties of the micellar solutions and may be exploited for uptake and targeted release of functional compounds. The small-angle neutron scattering data taken in this experiment not only show these structural changes in unprecedented detail, they also demonstrate the effects of an increasing salt concentration and reveal an as yet unexplained effect whereby the final structures are influenced by the addition rate of the base.

Experimental Details

The experimental set-up is shown in Figure 1a. For each measurement, a 100 mL, 3-necked round-bottomed flask was charged with 50 mL of D_2O and ~0.51 mL of polyoxyethylene(4.5) lauryl ether carboxylic acid surfactant (1 wt%, structure shown in Figure 1b, commercially known as AKYPO RLM 45 CA, Kao Corp., Japan). The solution was stirred and continuously circulated through a 1 mm path length flow-cell (Helma, Germany) positioned in the neutron beam, using a peristaltic pump (100 series, Williamson, UK) at a flow rate subsequently measured to be approximately 1 mL/s. Syringe pumps (NE-1010, New Era Pump Systems, USA) were used to dispense NaOH and HCl solutions (0.1 M in D_2O for the initial measurements and 1 M in D_2O for the hysteresis measurements). The syringe pumps were controlled remotely throughout the experiment via the NOMAD instrument control platform. The pH was measured by recording the potential difference over a pH electrode (via the analogue output port of an *F20* pH meter, Mettler Toledo, USA) and subsequently converting the result into a pH value by means of a previously performed calibration. To fully capture the structure of the micelles, three sample-to-detector distances were used (1.5 m, 8 m and 34 m) with a wavelength of 6 Å, giving a Q-range of 0.015-0.42 $Å^{-1}$. Three separate but related experiments were performed. The first consisted of a slow addition (12 mL over 2 hours) of 0.1 M NaOH to the aqueous surfactant solution. SANS was measured continuously (120 x 60s measurements) and the procedure was repeated under identical conditions at the three detector configurations. The second experiment consisted of a rapid addition (1.2 mL over 1.2 s) of 1 M NaOH to the aqueous surfactant solution at a detector distance of 8 m. The final experiment, to observe the hysteresis behaviour and effect of salt concentration, consisted of two successive additions of 1 M HCl and 1 M NaOH (1.2 mL over 24 mins, paused at 0.6 mL to allow for measurement at additional detector distances). In this case, SANS was measured continuously during addition at a detector distance of 8 m, and additionally at the 1.5 m and 34 m configurations at the beginning, end and midway through each addition.

Preliminary Results

From the fast addition of NaOH to the surfactant solution, it was observed that the morphological changes of the self-assembled structures occurs rapidly. The pH measured at the electrode in the round-bottomed flask changed instantaneously on addition of the NaOH (within the 1 s time resolution of the measurement, see Figure 3a). The form of the azimuthally-averaged scattering data changed over approximately 6 s and then remained constant, as shown in Figure 3b. As the time taken for the sample solution to complete one circulation of the flow-loop is also ~ 6 s, the period over which the scattering changes is most probably due to the gradual homogenisation of the sample solution as opposed to the self-assembly kinetics of the surfactant.

Analysis of all of the datasets has not yet been completed, however a number of noteworthy trends can already be identified. With regards to the morphology of the aggregates, it can be seen from Figures 3b and 4a that at low pH (i.e. before addition of NaOH), the surfactant molecules self-assemble into large vesicle- or bilayer-type structures with a Q^{-2} dependence. As the pH increases, the morphology gradually evolves to favour smaller structures, most likely spherical micelles. These changes occur almost exclusively at low pH; the form of the scattering changes significantly between pH 3 and pH 7 but thereafter remains constant up to pH 12. These observations are consistent with recent, as-yet unpublished, one-off measurements on the same system.

The structural changes observed over successive additions of NaOH and HCl, as shown in Figure 4b, indicate that as the concentration of NaCl in the surfactant solution increases, the vesicle structures formed at low pH become more regular, as can be seen by the appearance of higher-order oscillations. In contrast, no significant effects were observed of increasing salt concentration on the morphology of the spherical micelles formed at high pH.

Finally, a comparison of the scattering from high pH solutions formed by fast and slow addition of NaOH respectively, yielded a surprising effect. In Figure 5, it can be seen that the solution where the NaOH was added quickly, one broad structure factor peak is observed, indicating a single, polydisperse population of charged micelles. Where the NaOH is added over the course of two hours however, an upturn in the gradient is observed at low-Q, indicating the presence of a significant population of larger aggregates. No significant changes were observed when these samples were remeasured after 24 hours which, given the expected rapid dynamics of the surfactant molecules, indicates that both scenarios are at least meta-stable. It is not immediately clear why this should be the case, however it may arise from impurities in the surfactant material or significant polydispersity in the ethylene oxide or alkyl chain lengths of the surfactant molecules. This phenomenon is currently being examined further via purification of the surfactant material as well as further measurements using static and dynamic light scattering.

Conclusions

Using a prototype continuous-flow setup, it was possible to perform an in-situ titration reaction on an aqueous surfactant system that enabled us to follow the nanostructural evolution that occurs in response to changing pH. From a technical standpoint, the experiment was successful; it was possible to integrate the electrode and pumps into the NOMAD platform such that they could be controlled from the D11 workstation. Furthermore, useful information was gained with respect to the capabilities and limits of the set-up for various parameters such as pumping speed, addition rate and measurement duration. This information will be invaluable when designing the next iteration of the flow-cell and in-situ reaction sample environments. From a scientific perspective, although the surfactant system had been studied previously, the results of this experiment confirmed previous light scattering, TEM and SANS observations regarding the changing nanostructure with a much finer resolution in pH. It also revealed a number of previously unobserved phenomena such as the dependence of the final structures on the speed of NaOH addition, providing an interesting avenue for further investigation.

References

[1] Renoncourt, A. *et al*. *ChemPhysChem*, **2006**, 7(9), 1892-96 ; [2] Vlachy N. *et al*. *Langmuir*, **2008**, 24 (18), 9983–88 ; [3] Chiappisi L, *et al*. *Langmuir*, **2014**, 30(35), 10608-16.

Figures

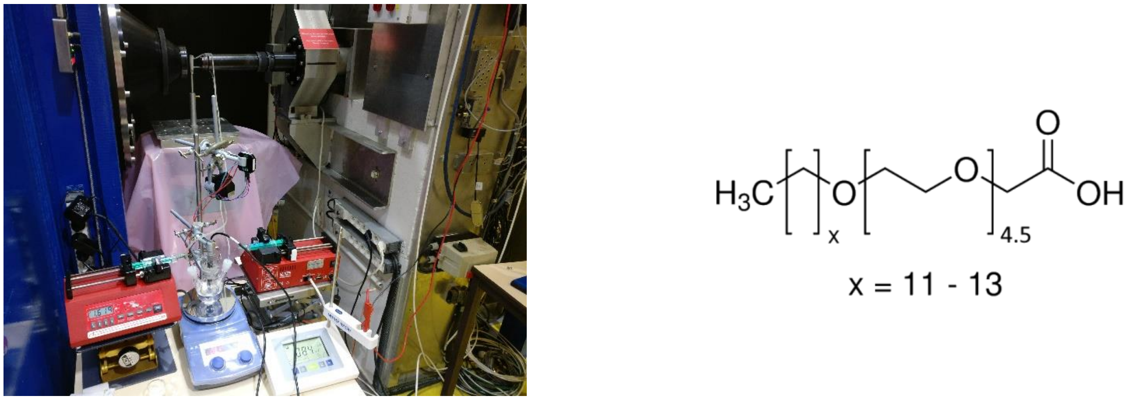

Figure 1 (a) Photograph of the experimental set-up on the D11 instrument. (b) Chemical structure of the polyoxyethylene lauryl ether carboxylic acid surfactant used in this experiment.

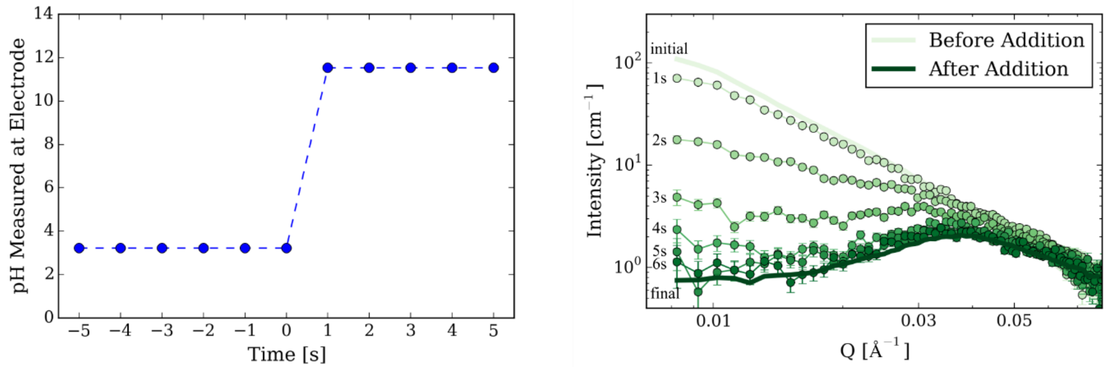

Figure 2 (a) Recorded pH before and after fast addition of NaOH (1.2 mL 1 M NaOH added over 1.2 s), (b) azimuthally averaged scattering data showing the evolution of the nanostructure after addition of NaOH. Solid lines represent data averaged over the 30 s before addition and 30 s after the structure has equilibrated (i.e. 7-36 s after addition).

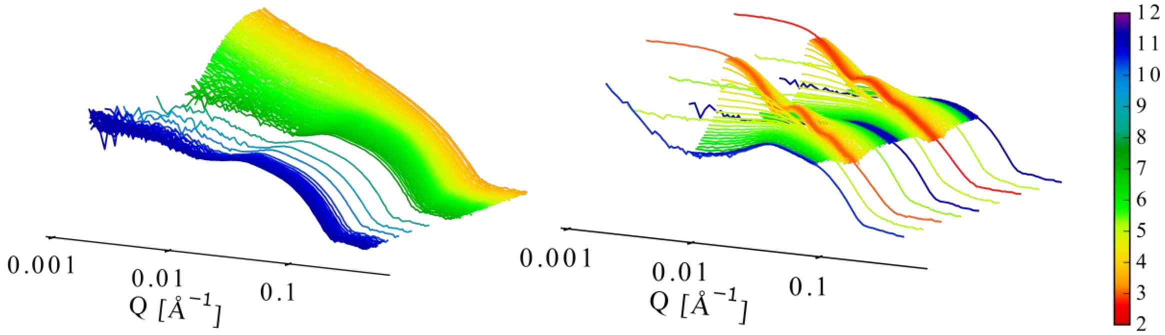

Figure 3 Azimuthally averaged scattering data showing (a) the structural evolution occurring on slow addition of dilute NaOH, (b) the structural changes that occur with subsequent successive additions of HCl and NaOH (with a consequent gradual increase in the concentration of NaCl). The colour of the lines represents the pH at which the measurement was conducted.

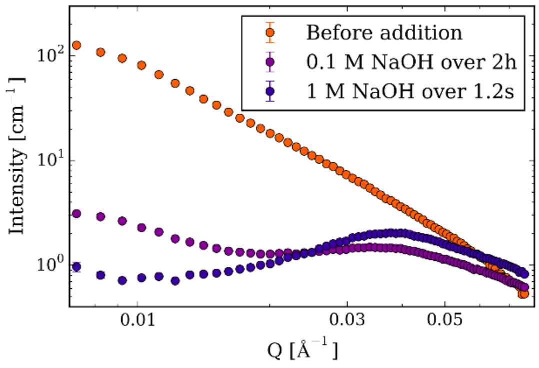

Figure 4 Azimuthally averaged scattering data from surfactant solutions after fast and slow addition of concentrated and dilute NaOH, respectively.