# Experimental report

25/10/2018

**Proposal:** **9-12-540** **Council:** 4/2018

**Title:** Direct Measure of the Surface Excess and Structure of Photo-Switchable Molecules at Air-Water Interfaces

**Research area:** Chemistry

**This proposal is a new proposal**

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**Samples:**
arylazopyrazole tetraethylene glycol carboxylic acid
azobenzene triethyl ammonium bromide
butyl arylazopyrazole sulfonate

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| FIGARO Adsorption troughs | 3 | 3 | 11/09/2018 | 14/09/2018 |

## Abstract:

The molecular properties of photo-responsive foams attract considerable interest. Foams are inherently interface-controlled materials and their ability to respond to light stimuli is coupled with the ability to change the interfacial molecular structure. Because light can be localized in time and space, photo-responsive interfaces offer exciting new possibilities to control foams in four dimensions. In order to improve the switching ability of air-water interfaces - as a major building block of aqueous foam - we have performed precision synthesis of photo-switches such as arylazopyrazoles (AAP). These are superior to azobenzene surfactants with increased thermal stability and a favorable photo-stationary state. Surface tension and vibrational sum-frequency generation (SFG) experiments have shown the AAP's ability to change both the surface tension and the charging state reversibly by photo-isomerization. Direct quantitative information on the change in surface excess and structure under light irradiation is missing so far and is gained by the proposed NR experiments. Further, we plan to prepare a manuscript where we add complementary information from SFG and tensiometry.

# Experimental Report: Direct Measure of the Surface Excess and Structure of Photo-Switchable Molecules at Air-Water Interfaces (#9-12-540)

## Introduction

Foams are ubiquitous in our daily lives. In order to formulate foam with specific properties, its structure must be controlled at the molecular level. In this report, we introduce a new class of photo-switchable surfactants and their 2D assemblies, which make the interface as well as the macroscopic foam responsive to light irradiation. This opens exciting new possibilities for foams such as self-healing capabilities. We have synthesized amphiphilic arylazopyrazoles (AAP) which are superior analogues of azobenzene (AB) surfactants. It is well known that the two configurational isomers of these photosurfactants, *E* and *Z* respectively, have different behaviour in the bulk. Our tensiometry data indicate that for both classes of surfactants the *E* isomer is more surface active. Furthermore, foams from AB and AAP photo-surfactants can be destabilized in situ when illuminated with UV light allowing high spatiotemporal control of the stimulus. However surface tension measurements alone do not give a direct measure of the surface excess. To the best of our knowledge, direct measurements of the interfacial changes by photoswitchable surfactants under visible/UV light irradiation with respect to molecular composition (surface excess/structure) using NR have not been reported so far.

## Experiment

In this work, we proposed to understand the behaviour of these systems at the air-water interface using neutron reflectometry on the FIGARO reflectometer at the ILL. The plan was to look at 5 different surfactants: AAP-$BuSO_3$ and $d_{13}$-AAP-$BuSO_3$ (0.1 mM, 0.5 and 1.5 mM), AAP-$E_4$ (pH 4: 0.5 mM and 1.5 mM, pH 7: 0.7 mM and 4 mM), AAP-$E_8$ (pH 4: 0.3 mM and pH 6: 0.75 mM) and Azo-TEAB (10 and 20 mM) (see structures in the original proposal). The key to the success of this proposal was the technical adaption of FIGARO's standard 6-position adsorption troughs to contain both green and UV LEDs. These were positioned on extended mounts immediately above the air-water interface whilst care was taken not to obstruct the neutron beam. A last minute intervention by the instrument technician, Mr. Wood, was much appreciated in the realization of this setup.

An experimental plan was devised where after setup/direct beams/calibrations (5–6 h), an initial test run (4–5 h) was carried out on 3 surfactant samples in air contrast matched water (ACMW) and the same 3 samples in $D_2O$ in order to assess the magnitude of the changes at low Q in ACMW and high Q in $D_2O$. This first part was organized in order to see for real which parts of the data changed the most when the LEDs were switched from green to UV. Three different surfactants (APP-$BuSO_3$, AAP-$E_4$ and AAP-$E_8$) were chosen at the highest of the planned concentrations in order to minimize kinetic effects. It was shown that the biggest effects in the data were clearly exhibited from the first angle (low Q) in ACMW. The primary experiment then comprised 5 runs of the 6-position sample changer with samples both in ACMW and in $D_2O$. Initially, each set of 3 samples in ACMW was scanned at low Q sequentially for 1.0 – 1.5 h while the samples equilibrated during exposure to green light. Next a full structural analysis was performed (full Q for all 6 samples taking 4 h), after this the LEDs were switched from green to UV. From our prior surface tension measurements we know the switch from the *E*- to the *Z* structure is (comparably to the other way switching) fast and complete after 10 to 15 min. Here after a fully structural characterization of this state was recorded for 4 h. Each sample was irradiated and switched individually from UV to green light, and kinetic data of 20-s acquisition were recorded for 10 min. These key data provided the first ever resolution of the kinetic switching of the *Z* to *E* configurations of the surfactants in monolayers at the air-water interface. Due to well calculated time, a repetitive fast switching experiment of a monolayer of the custom-deuterated surfactant ($d_{13}$-AAP-

BuSO$_3$ at a concentration of 0.25 mM) could be performed where the LED were switched twice from green to UV and once form UV to green.

**Preliminary Data Analysis**

The adsorption of the different photo surfactants is shown in Fig. 1. The equilibrium is reached for all samples in less than an hour which is much faster than the prior made suggestion based on the surface tension data (see the original proposal). For the AAP-BuSO$_3$ the maximum surface excess in this experiment is at 1.5 mM and not at the highest conc. of 10 mM, which was expected. This may be related to increasing formation of micelles within higher concentrations to the detriment of adsorption at the air water interface. The AAP-E$_4$ needs around 30 min to get to an equilibrium at low concentration, whereas at high concentration it seems that it is in equilibrium in around 5 min. For the AAP-E$_8$ the equilibrium is faster reached for a lower pH. Azo-TEAB reached the equilibrium at a lower concentration faster, what seems to be surprising, compared to the tensiometry data. However, surface tension might be at later adsorption times dominated by reordering processes at the interface which do not change the surface excess significantly.

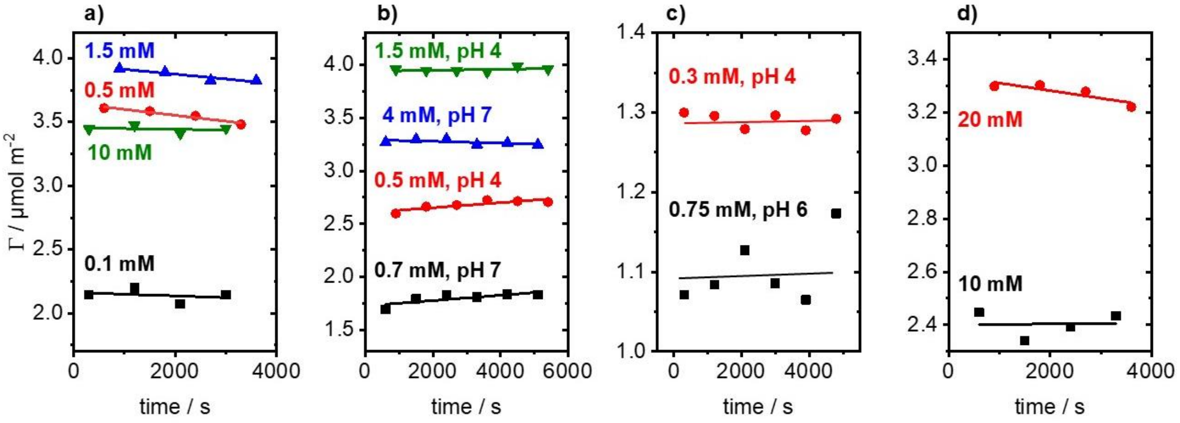

Fig 1. *Surface excess as a function of time for the adsorption process of the different photo switchable surfactants: AAP-BuSO$_3$ (a), AAP-E$_4$ (b), AAP-E$_8$ (c) and Azo-TEAB (d).*

We could demonstrate with this FIGARO experiment the dramatic changes in the surface excess of the deuterated butyl arylazopyrazole sulfonate surfactants (d$_{13}$-AAP-BuSO$_3$, Fig. 2a) following irradiation with UV vs. green light. This direct information has so far been inaccessible because the techniques applied to date (such as surface tensiometry and vibrational sum-frequency generation spectroscopy (SFG)) are indirect measurement methods for the interfacial amounts and structure. In our NR experiment, we were able to resolve the changes in the surface excess of different molecules on a sub-minute time scale and at a relatively moderate bulk concentration of 0.25 mM. The figure shows that the surface excess of the deuterated surfactant changes from ~3.5 µmol/m$^2$ (~2 molecules/nm$^2$) to values under 0.7 µmol/m$^2$ (~0.4 molecules/nm$^2$) (Fig. 2a) within less than 120 s (UV to green) and 10 min (green to UV). This unprecedented result was unexpected because the other techniques (surface tensiometry and SFG) show a different behaviour where the switch from green to UV light has a much faster kinetic than the switch from UV to green light. Furthermore we could prove once again that the switching between the *E* and *Z* isomers is reversible. In Fig. 2b the back switch from UV to green light for the nondeuterated AAP-BuSO$_3$ is shown, and indicates that the change of the surface excess is lower, but also around 1 µmol/m$^2$.

In fact, our NR experiment of other AAP derivatives like AAP-E$_4$ and AAP-E$_8$ show much smaller changes and a dramatically reduced responsiveness of the air-water interface under light irradiation (see Fig. 2b vs. 2c and d), which raised the question of how chemical modification of a surfactant can result in such dramatic changes in the surface and foaming properties of photo-responsive materials (Azo-TEAB not shown, have a similar trend). This question has not been addressed to date to our knowledge, and as such we have worked quickly to submit a continuation proposal for the deadline that occurred on the working day following the end of our experiment.

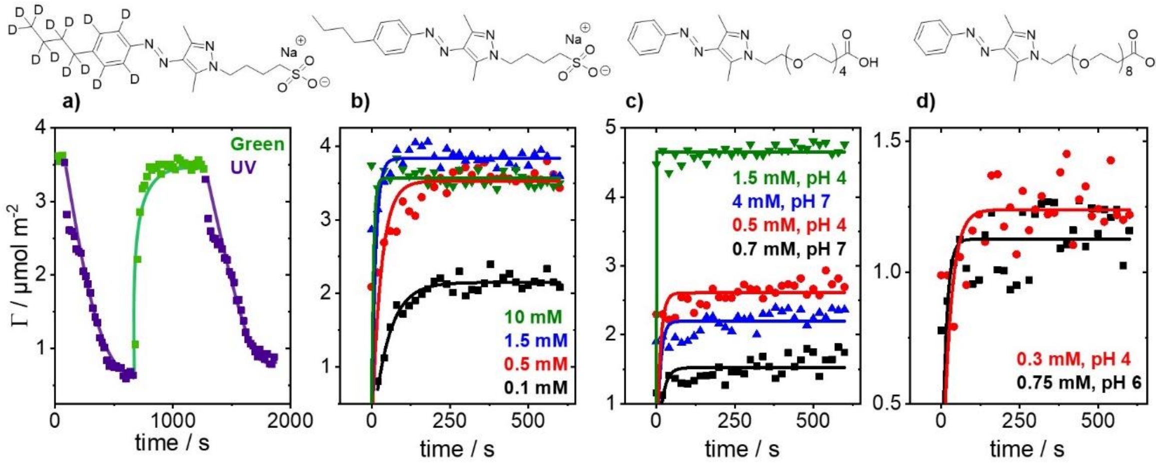

Fig. 2. *Surface excess Γ of photo-switchable surfactants from neutron reflectometry (NR) as determined from our experiments. a) Switching kinetics of a deuterated butylarylazopyrazole sulfonate ($d_{13}$-AAP-$BuSO_3$, 0.25 mM) by changing the light irradiation from UV to green and back to UV. Interfacial kinetics of Γ from NR for the back switch from UV to green irradiation for b) AAP-$BuSO_3$ c) AAP-$E_4$ and d) AAP-$E_8$. Solid lines are guides to the eye (a) or FITs from Equation 1 (b-d).*

Furthermore we fit the surface excess data from the switch from UV to green with: $\Gamma = \Gamma_\infty (1-e^{(-kt)})$. Whereas Γ the surface excess at the time t, $\Gamma_\infty$ the surface excess for t → ∞ and k the kinetic constant, which results are presented in Tab. 1. The kinetic data for AAP-$BuSO_3$ shows, that with increasing the concentration the kinetic constant increase (from 0.02 $s^{-1}$ at 0.1 mM to 0.17 $s^{-1}$ at 10 mM), which means that the readsorption process is faster for higher concentrations. The kinetic constants for the AAP-$E_4$ and AAP-$E_8$ are all in a same region around 0.06 $s^{-1}$, which makes sense because the surface excess for this samples are also in a same region (see. Fig. 2 c) and d)). At a concentration of 1.5 mM at pH4 the AAP-$E_4$ shows a very high kinetic constant of 5.51 $s^{-1}$, which can explain by the very high surface excess of around 4.5 µmol/m², indicating a multilayer surface. The two samples of the Azo-TEAB (10 and 20 mM) show kinetic constants around 0.17 $s^{-1}$, which are also in good comparison with the 10 mM high concentration of AAP-$BuSO_3$.

Tab. 1. *Kinetic constants k for the different surfactants.*

| | **AAP-$BuSO_3$** | | | | **AAP-$E_4$** | | | | **AAP-$E_8$** | | **Azo-TEAB** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| c /mM | 0.1 | 0.5 | 1.5 | 10 | 0.7 pH 7 | 0.5, pH 4 | 4, pH 7 | 1.5, pH 4 | 0.75, pH 6 | 0.3, pH 4 | 10 | 20 |
| k / $s^{-1}$ | 0.02 | 0.03 | 0.08 | 0.17 | 0.06 | 0.09 | 0.09 | 5.51 | 0.07 | 0.04 | 0.19 | 0.15 |

Compared to other AAP derivatives at the air-water interface, the origin of the switchability of AAP-$BuSO_3$, which is accompanied by similar dramatic change in foam stability with foam half-life times of > 5 h (green) and < 300 s (UV), is so far not understood on a molecular level. In order to proceed, a molecular level understanding of the very high switchability of AAP-$BuSO_3$ is required. The continuation proposal that we have submitted will give us a chance of resolving this issue and writing these unique results into a high impact communication and a thorough follow-up paper.