Experimental report

10/03/2020

Proposal:	**9-10-1573**	**Council:**	10/2018

Title: Structure and dynamic changes in the surface excess of arylazopyrazole surfactants at the air-water interface

Research area: Chemistry

This proposal is a continuation of 9-12-540

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Samples:
AAP-HSO3
AAP-OcSO3
AAP-BuSO3

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	2	3	22/07/2019 16/01/2020	24/07/2019 17/01/2020

Abstract:

The molecular properties of photo-responsive foams attract considerable interest. In order to improve the switching ability of the air-water interfaces, which are inherent to the stability of foams, we have synthesized a series of molecular arylazopyrazoles (AAP) photo-switches. In our recent experiment on FIGARO, we have demonstrated for the first time dramatic changes in the surface excess of AAPs following irradiation with UV vs. green light. In fact we were able to resolve their changes on a sub-minute time scale even for non-deuterated molecules. This raised the question of how chemical modification to a surfactant can result in such clear changes in the surface and foaming properties of photo-responsive materials. Here we propose to resolve unambiguously these effects by systematic chemical variations of the residues (octyl, butyl, H) at the arylazopyrazole center. For that, detailed quantitative information on the changes in surface excess in real time and the equilibrium structures of the three new molecules under light irradiation is required. This information can only be delivered by neutron reflectometry experiments, optimized on the FIGARO reflectometer at the ILL.

Experimental Report: Structure and dynamic changes of arylazopyrazole surfactants at the air-water interface (#9-10-1573)

Introduction

Responsive interfaces and surfaces have great potential and are required for adaptive materials such as foams with self-healing properties. Aqueous foams can be stabilized with surfactants, polyelectrolytes or proteins as molecular building blocks. To understand and control foam stability it is essential to characterise the foam structure and its major hierarchical elements such as the air-water interface at a molecular level. The responsiveness can be reached with external stimuli such as light, temperature, magnetic or electric fields etc. The use of light is advantageous because it offer spatio-temporal control of soft matter interfaces. In this report, we show photo-switchable surfactants that render the air-water interface and with this also aqueous foams responsive to light irradiation. We have synthesized amphiphilic arylazopyrazoles (AAP) and azobenzene (AB) surfactants. These surfactants can be switched between their E and Z conformations using light with wavelengths of 520 nm and 365 nm, respectively. Our tensiometry data indicate that for both classes of surfactants the *E* isomer is more surface active than the *Z*. Using sum-frequency generation (SFG) we observed a decrease of the C-H and O-H bands which indicates a desorption of the molecules from the air-water interface. Furthermore, foams from AB and AAP photo-surfactants can be destabilized *in situ* when irradiated with UV light allowing for substantial control of the stimulus. However, surface tension measurements alone do not provide a direct measure of the surface excess. Only recently we were able to publish our recent findings where neutron reflectometry helped to elucidate a unique monolayer to bilayer transition of AAP surfactants at the air-water interface and its role on foam stability and light-induced manipulation of colloidal systems (*Chem. Sci.* 11, 2085-2092 (2020)).

Experiment

In this current work, we have analysed several new photoswitchable surfactants, which were previously not available with the focus on a further understanding of their behaviour in different conformations at the air-water interface using neutron reflectometry at the FIGARO experiment. During earlier experiments we observed a significant (but useful, see *Chem. Sci.* 11, 2085-2092 (2020)) mismatch between results from SFG and NR. In fact, we have shown earlier that the mismatch can be used to address molecular ordering as well as coverage and structure changes at the interface independently which is not easily possible with the results of from SFG or NR alone. Therefore, we believe that the combination of NR with SFG can be a powerful approach to reveal equilibrium and non-equilibrium properties of photo-switchable amphiphiles at the air-water interface. For that, we decided to spend one part of the experimental time for structural measurements of sample with distinct concentrations and the other on kinetic measurements to determine the surface excess for several concentrations under different illuminations. During our experiment we have successfully recorded the following couple of structural datasets: H-AAP-C_4S (7 mM), butyl-AAP-C_4-S (6 mM) octyl-AAP-C_4-S. Moreover we determined the surface excess for a range of concentrations for the five different surfactants: H-AAP-C_4-S: (1, 10, 30, 50, 75 mM), Butyl-AAP-C_4-S (0.02, 0.05, 6 mM), Octyl-AAP-C_4S (0.002, 0.005, 0.01, 0.05, 0.5, 5 mM), AAP-TB (0.1, 1, 7, 15, 30, 40 mM) and Azo-TB (0.1, 1, 7, 30 mM)). The key to the success of this experiment 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. Although some LEDs of our setup malfunctioned just before the end of the experiment we were able to complete the experiment as planned. Moreover the successful synthesis of deuterated surfactants was crucial to the recording of structural data in this experiment.

Note that this experiment was split up into two beam times because of problems with the instrument during the initially planned experimental run. During the first stay these problems compromised both the acquisition of data and the quality of recorded data itself. Nevertheless during the second part of this proposal in January 2020 we successfully completed the experiments.

The procedure during the experiments was as described in the following. First setup, direct beams and calibration runs were measured (5–6 h). For the photoswitchable surfactants it was shown in our first beam time that the biggest effects in the data were clearly exhibited from the first angle (low Q) in ACMW. Initially, each set of samples in ACMW was scanned at low Q sequentially for 1.0 – 1.5 h for kinetic analysis while the samples equilibrated during exposure to green light. Next a full structural analysis was performed and after this the LEDs were switched from green to UV, which causes the surfactants to photo-isomerize from the *E* to the *Z* conformation. After switching the light irradiation, the samples were again scanned in the low Q approach to ensure an equilibrium state was reached at the air-water interface. Subsequently, a full structural analysis was conducted for all samples. From our prior surface tension measurements we did know the switching kinetics at the air-water interface at least in terms of dynamic surface tension changes. From that we concluded that the change in conformation from the *E* to the *Z* state, was comparably fast and was completed after >10 min. Note that the switching from the Z to the E state is substantially slower at the air-water interface, which we have previously related to a slow self-assembly process of the surfactants at the interface. Once the interfaces were in equilibrium under UV irradiation, a full structural analysis was recorded for UV light conditions.

In addition, to recording structure data, isotherm data the surfactants which where dissolved in ACMW were recorded in a low Q approach For each sample the surface excess was determined at least 3 times after an equilibrium for the *E* as well as the *Z* conformation was reached.

Preliminary Data Analysis

In Figure 1 the surface excess Γ at different bulk concentrations and for the different surfactants under are presented for the surfactants being in the *E* and the *Z* state (green vs UV irradiation). As seen in the figure, the surface excess for the samples irradiated with green light is in all cases higher compared to UV irradiation. For example, the AAP-TB surfactant showed a maximum change 2.2 μmol/m^2 at a concentration of 7 mM. The decrease in Γ under UV light indicate a desorption of the surfactant from the air water interface of the surfactant. Also for the Azo-TB the surface excess is higher under green light irradiation compared to irradiation with UV light, but showy minor differences with a maximum change of 1.0 μmol/m^2.

Exemplary we have conducted a first analysis of the structural data recorded at the experiment. Here we analysed the development of the adlayer on a 6 mM solution of Butyl-AAP-C_4-S under both green and UV irradiation, which is depicted in Figure 2. A short inspection of both panels reveals the fact that no distinct changes within the reflectivity have been observed. This is in accordance with our SFG experiments were no change in the intensity of the S-O stretching vibration for this concentration were observed. Considering that the fitted layer thickness of these samples is equivalent to the length of the molecule we assume that due to a close packing of the surfactant molecules at the air water interface the photo isomerization is sterically hindered, locking the molecules in the *E* state.

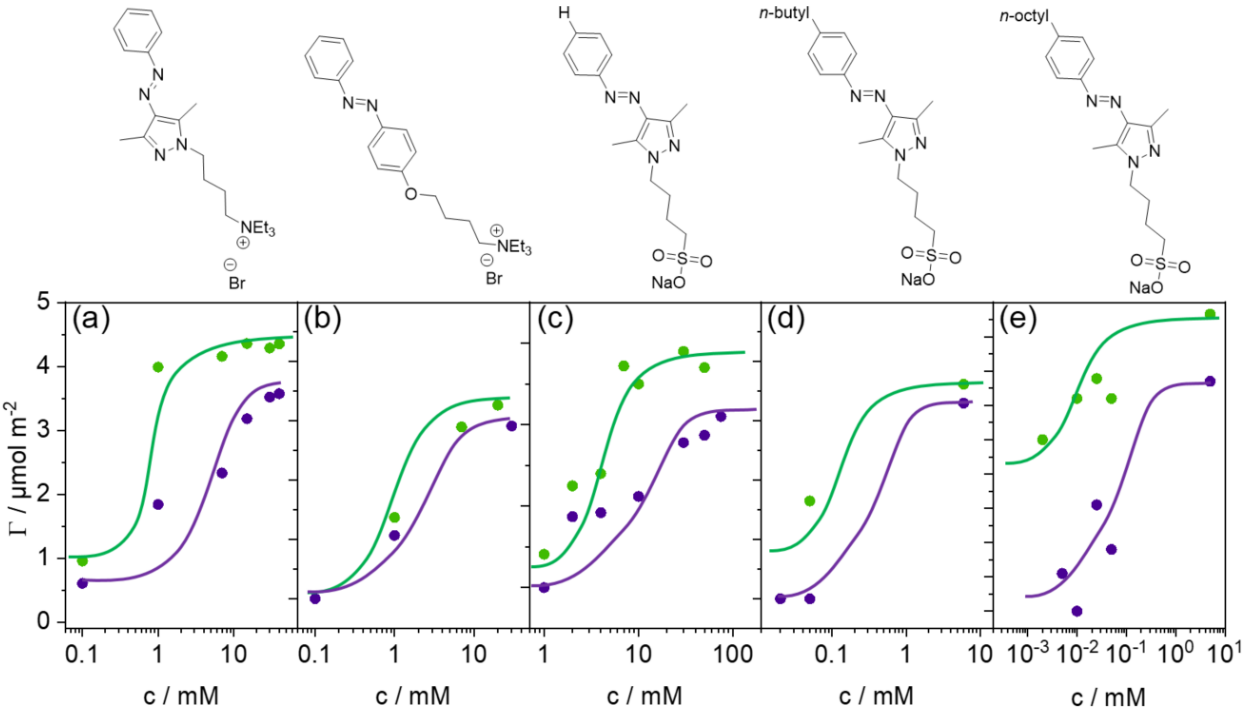

Figure 1 Molecular structure and surface excess at selected concentrations under green (green dots) and UV light (dark blue dots) for a) AAP-TB, b) Azo-TB, c) H-AAP-C_4-S, d) butyl-AAP-C_4-S and e) octyl-AAP-C_4-S. Solid lines in guide the eye. Note that in d) we present in this report only results that have been recorded during this experiment, but which are complemented by previous results.

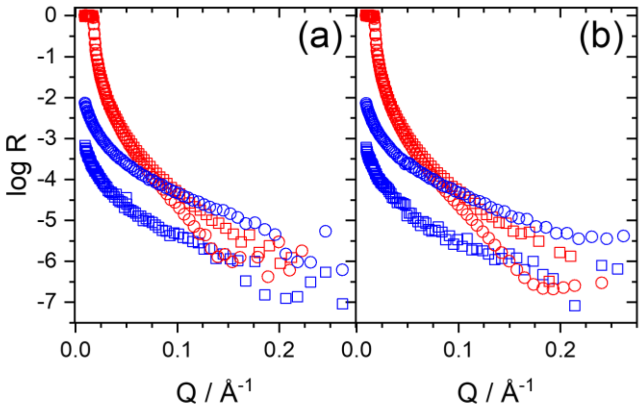

Figure 2 *Reflectivity curves for a set of 4 isotopic contrasts (hydrogeneous (open squares) and partially deuterated (open circles) surfactant in ACMW (blue) and D_2O (red)) of a 6 mM solution of butyl-AAP-C_4-S under irradiation with 520 nm wavelength (a) and 365 nm wavelength (b).*