Experimental Report

12/09/2014

Proposal: **TEST-2352** **Council:** 4/2014

Title: Surfactant/oil vapour interactions

This proposal is a new proposal

Researh Area:

Main proposer: **MILLER Reinhard**

Experimental Team: MILLER Reinhard

Local Contact: CAMPBELL Richard

Samples: D14-Hexane + Hexane
D2-Hexadecyltrimethyl ammonium bromide + Hexadecyltrimethyl ammonium bromide
D25-Sodium Dodecyl Sulfate + Sodium Dodecyl Sulfate

Instrument	Req. Days	All. Days	From	To
FIGARO	1	1	03/09/2014	04/09/2014

Abstract:

Test 2352 on Figaro – Experimental Report

Resolving the interfacial composition at the water/oil vapor interface

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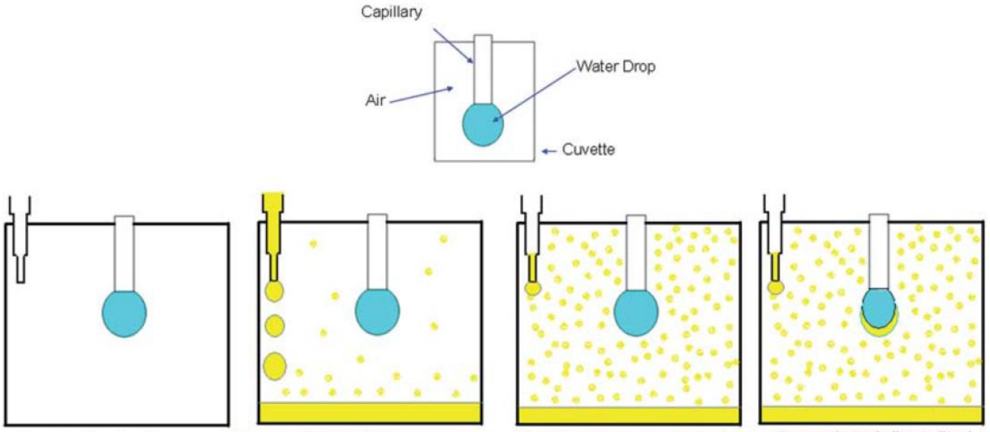
Wednesday 3rd September 2014

Scientific Background.

Surfactants are used in many processes and technologies, such as detergency and food processing as well as in the pharmaceutical and cosmetic industries. The importance of understanding the structure and composition of adsorption layers formed at interfaces has prompted prolonged and ongoing research efforts [1–4]. In comparison with the liquid/air and liquid/liquid interfaces, we have demonstrated recently that the liquid/oil vapor interface represents an intermediate state [5]. The adsorption of material at this interface is governed by the mutual interaction between surfactants and oil molecules [6–8]. So far just few papers have been dedicated to the thermodynamics of adsorption at water/oil vapor interfaces. The reason for this might be difficulties in performing the experiments and the technicalities of the experimental setups. As a result, there is quite a number of pending questions. A clear understanding of the molecular structure of the mixed surfactant/oil adsorption layer requires the development of suitable theoretical models backed by robust experimental data.

Previous Results: References 5–8.

We have worked recently on various aspects of surfactant adsorption at the water/oil vapor interface. We started by demonstrating that different short chain alkanes (pentane, hexane, heptane and octane) co-adsorb to surfactant monolayers at the water/oil vapor interface from a saturated vapor phase [5]. Measurements were carried out using drop profile analysis tensiometry and it was shown that the molecular adsorption transfers into condensation resulting in a thin alkane film at the drop surface. The experimental setup for the measurements is shown in figure 1.



A: water drop in air

B: hexane liquid injection, simultaneously evaporation is started

C: saturated cuvette atmosphere with alkane vapor

D: condensed alkane dimple on water drop surface

Figure 1. Experimental setup for the drop shape analysis measurements of surfactants at the liquid/oil vapor interface.

The co-adsorption from hexane vapor and aqueous surfactant solutions was then studied with respect to the surfactant concentration [6]. For sodium dodecyl sulfate (SDS) as well as dodecyltrimethyl-ammonium bromide (C_{12}TAB), remarkable decreases in surface tension were observed (see figure 2A). For dilute solutions, where there is almost no observable drop in surface tension in the absence of oil vapor, the mixed system resulted in different surface tension values by several mN/m (e.g. compare curves 2 and 3). For more concentrated solutions, the surface tension values were far lower than can be produced by single-component, single-chain hydrogenous surfactants alone (e.g. curve 6). The maximum effect results for solutions of intermediate concentration (e.g. curve 5).

We published a paper earlier this year with results on the co-adsorption of hexane with four members of the cationic surfactant C_nTAB family for n=10, 12, 14 and 16 [7]. For three surfactants we have also investigated the effect of hexane vapor pressure on the co-adsorption process [8]. The isotherms obtained in the various studies were described by a theoretical model which assumes competitive adsorption of surfactant and hexane from the vapor phase (see figure 2B). The model calculations allow calculation of the amounts of surfactant and hexane at the interface. Nevertheless to date these calculations of the equilibrium values of the interfacial composition have not been validated experimentally.

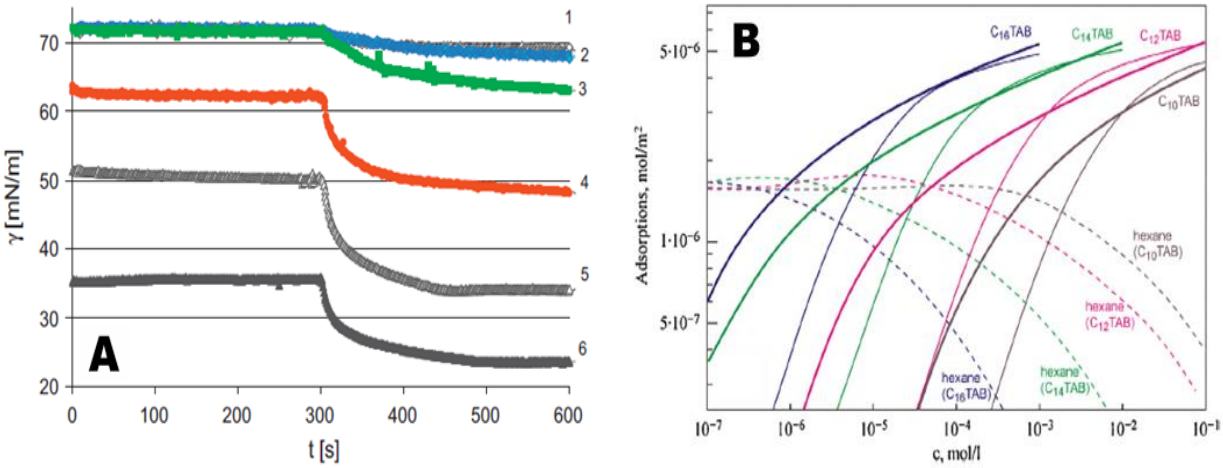


Figure 2. (**A**) SDS monolayers at the liquid/air interface exposed to hexane vapor at t = 300 s, where the surfactant concentrations are (1) 0, (2) 10^{-6}, (3) 10^{-5}, (4) 10^{-4}, (5) 10^{-3} and (6) 10^{-2} M [6]; (**B**) calculated dependencies on the co-adsorption of C_nTAB surfactants (full lines) with hexane vapor (dashed) [7].

Recent Advance: Figaro Test Experiment 2352.

Following presentation of this work at the *20th Surfactants in Solution* meeting in July this year, the Figaro instrument responsible described how high flux neutron reflectivity measurements at low Q, contrast matching the surfactant then the hexane in turn to air, could reveal the interfacial composition for the experimental validation of the thermodynamic models. This test experiment was offered, which went ahead on Wednesday 3rd September 2014. For this experiment, 5 grams of deuterated hexane had been purchased, and it is highly volatile which meant that the sample handling methods used had to be very careful. The main unknown in this experiment was the effects of the different experimental conditions, i.e., changing from a small aqueous droplet exposed to a large surface area of hexane to a very large planar water/air interface (~ 100 cm^2) exposed to a much smaller surface area of hexane.

Run 1. The first experiment was to expose 0.5 g of deuterated hexane to air contrast matched water, which was known to reduce the surface tension by several mN/m. The scattering excess was measured at low Q for 1 hr. From the expected change in surface tension it was predicted that a hexane monolayer of ~ 40% coverage would form, and this should be easily resolved on FIGARO. However, no effect on the data was seen. So we concluded that the experimental conditions were sufficiently different that the saturated oil vapor phase had not formed.

Run 2. The second experiment was to expose 1 g of hydrogenous hexane to a deuterated DTAB monolayer of intermediate coverage (0.1 mM). This measurement was most sensitive to the amount of surfactant at the interface and only weakly sensitive to the amount of hexane. The hypothesis under test was that if the amount of surfactant at the interface changed at all then we would be able to measure it without the consumption of more deuterated hexane. This experiment showed a clear reduction in the surfactant surface excess, which could be explained either by a small reduction in the amount of surfactant at the interface, a large increase in the amount of hexane at the interface, or some combination thereof. Therefore we concluded that with 1 g of hexane we could form the saturated vapor phase required for the interaction with aqueous surfactant monolayers.

Run 3. Following this positive result, we measured the interaction of 1 g of deuterated hexane on a contrast matched $C_{16}TAB$ solution (again 0.1 mM). This measurement is only sensitive to the amount of deuterated hexane at the interface, and with time the adsorption of the oil into the surface monolayer was resolved. As we approached the overnight runs, we knew we needed measurements on the same systems in different isotopic contrasts to reveal the kinetic changes in the interfacial composition.

Overnight runs. With 6 positions on the sample changer available, we decided to measure the following samples all at approximately one tenth of the respective critical micelle concentrations:

(1) 1 mM contrast matched C_{12}TAB with deuterated hexane in air contrast matched water
(2) 1 mM deuterated C_{12}TAB with hydrogenous hexane in air contrast matched water
(3) 0.1 mM contrast matched C_{16}TAB with deuterated hexane in air contrast matched water
(4) 0.1 mM deuterated C_{16}TAB with hydrogenous hexane in air contrast matched water
(5) 1 mM hydrogenous SDS with deuterated hexane in air contrast matched water**
(6) 1 mM deuterated SDS with hydrogenous hexane in air contrast matched water

{** Note that it is not possible to match SDS in contrast to air because the hydrogenous form has a positive scattering length density}

The surface composition of the interaction of hexane with three different surfactant monolayers was successfully revealed (see figure 3). The data show unequivocally that the reduction in surface excess results from competition in a mixed monolayer: the surfactant surface excess drops rather than a converse, synergistic effect where the presence of the hexane brings more surfactant to the interface. The green lines denote when the trough lids were removed demonstrating the reversibility of the interaction. With these exciting preliminary results proving the feasibility and potential of the Figaro measurements, we are now in a position to go ahead with a systematic study.

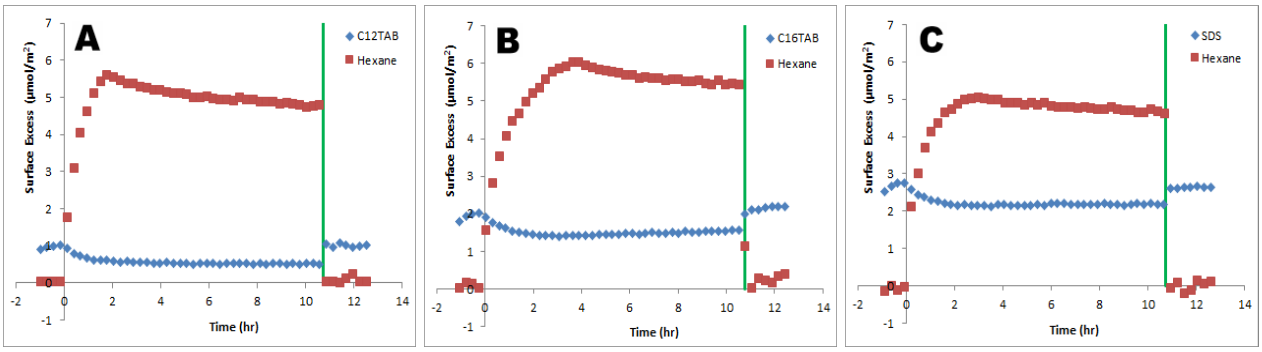


Figure 3. Interfacial composition for the interaction of hexane vapor with monolayers from solutions of (**A**) 1 mM C_{12}TAB, (**B**) 0.1 mM C_{16}TAB and (**C**) 1 mM SDS as revealed recently on Figaro.

Proposed Figaro Continuation Experiment.

In the autumn 2014 proposal deadline, we will apply for a continuation experiment. As we have published a significant body of surface tension data at the liquid/oil vapor interface, have applied theoretical models to the results, and have demonstrated the capability of Figaro to provide experimentally the missing interfacial composition, we feel that we are now in a position to propose an ambitious and systematic set of measurements. The proposal will concern measurements on 5 systems: C_{10}TAB, C_{12}TAB, C_{14}TAB, C_{16}TAB (cf. [7]) and SDS (cf. [6]), and in each case 5 surfactant concentrations from very dilute to above the cmc will be chosen (cf. figure 2A). These results will be used for the novel validation and optimization of the existing thermodynamic and elaboration of kinetic models of surfactant interactions at the liquid/oil vapor interface.

References.

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