Experimental report

23/08/2022

Proposal:	**9-12-652**	**Council:**	4/2021
Title:	Remote control of hydrophobic interactions between PDADMAC and arylazopyrazole sulfonate surfactants at the air-water interface		
Research area:	Chemistry		

This proposal is a continuation of 9-11-1984

Main proposer:	**Bjoern BRAUNSCHWEIG**
Experimental team:	Christian HONNIGFORT Michael HARDT
Local contacts:	Philipp GUTFREUND

Samples: Poly(diallyldimethylammonium chloride)
butyl-arylazopyrole sulfonate
octyl-arylazopyrole sulfonate

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	3	3	10/09/2021	13/09/2021

Abstract:

In this continuation proposal, we plan to address mixtures of polydiallyldimethylammonium chloride (PDADMAC) with two photoswitchable surfactants of varying hydrophobicity: butyl-arylazopyrazole sulfonate (butyl-AAP), which we have started to study previously, and octyl-AAP, which is new. Preliminary work shows that E/Z switching can lead to substantial changes in behavior in the bulk and at interfaces. Using neutron reflectometry (NR), we have started to exploit non-equilibrium aspects of polyelectrolyte/AAP mixtures by adapting them into responsive systems through resolving their switching ability, interfacial composition and structural changes at the air-water interface as a function of the bulk mixing ratio and light irradiation. Additional NR data involving custom-made deuterated surfactants over the full-Q range are required to complete the experimental objectives of proposal #9-11-1984 and include the neutron data in a planned publication, while unique molecular level details on the role of hydrophobic interaction in PDADMAC/AAP binding are proposed to support an additional publication focused on a comparison of the behavior of the butyl-AAP vs octyl-AAP systems.

Experiment Report: Remote Control of hydrophobic interactions between PDADMAC and arylazopyrazole sulfonate surfactants at the air water interface.

Introduction

Active surfaces and interfaces which can respond to external stimuli such as light or temperature and can change their chemistry on demand have great potential to serve as hierarchical elements for responsive functional materials such as foams. In addition, they can be useful to develop adaptive materials with self-healing or self-learning functions. In the previous experiment #9-11-1984 we initially addressed two photoswitchable polyelectrolyte/surfactant (P/S) systems that show remarkably changes in the bulk and at the interface upon light irradiation. One of the two systems is now published in *ACS Applied Materials and Interfaces*.[1] In experiment #9-12-652 we expand the results of the previous experiment by addressing polydiallyldimethyl ammonium chloride (PDADMAC)/surfactant mixtures with two now two photoswitchable arylazopyrazole (C_nAAP) surfactants which differ in their hydrophobic character. Both surfactants were studied without the presence of polyelectrolytes in previous FIGARO experiments using the combination of NR and SFG spectroscopy. The behavior of the first anionic surfactant namely the butyl-arylazopyrazole sulfonate (C_4AAP) and its mixtures with the biopolymer hydroxypropyl cellulose were published elsewhere.[2,3] The properties of the second surfactant, the octyl-arylazopyrazole sulfonate (C_8AAP), are currently part of a manuscript that is in preparation. Both surfactants can undergo *E/Z* photo-isomerization reactions when irradiated with 520 nm (green) light and 365 nm (UV) light which is used to change their interfacial behavior remotely. In particular, for C_4AAP previous NR and SFG experiments have suggested that a monolayer to bilayer transition takes place.[3]

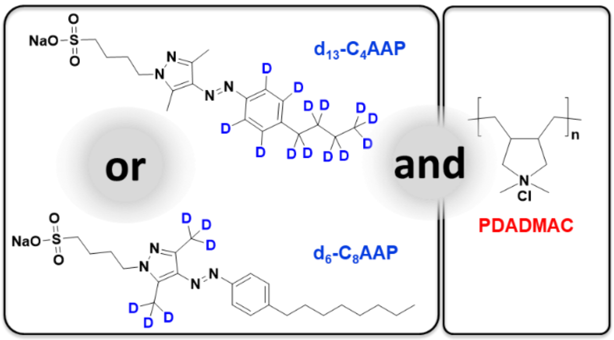

Fig. 1 Molecular structure of the C_nAAP/PDADMAC systems that were investigated. For clarity and illustration of the deuterated positions only the deuterated analogues are shown.

In experiment # 9-12.562, we have studied several mixing ratios for both C_nAAP/PDADMAC systems which complement the results of the previous study # 9-11-1984. The chemical structure of the molecules that were used in the experiment are shown in Fig. 1. For simplicity, only the deuterated molecules are shown while also their hydrogenated analogues were synthesized and used within this experiment. The presence of deuterated surfactants is crucial for this experiment as it allows the resolution of interfacial structure and surface excess for both, surfactants and polyelectrolytes. This can be used to qualitatively determine the interfacial charging state and can be compared to the information from complementary SFG spectroscopy which also provide a qualitative measure of interfacial charging.[4] In addition, the bulk aggregation and particle formation was studied using dynamic light scattering (DLS) and the aggregate charge was determined by addressing the electrophoretic mobility. These results can be qualitatively compared to the interfacial structure as a function of polyelectrolyte concentration. Clearly, the use of photo-switchable surfactants allows us to change bulk and interfacial properties such as composition and the interfacial charging state remotely by light irradiation. It was the aim of experiment #9-12-652 to further understand the structural information on air-water interfaces decorated with the P/S aggregates which could complement the information gathered in experiment #9-11-1984 and further to resolve whether the polymer/surfactant interactions can be tuned by molecular design, i.e. by introducing octyl-substituents at the surfactants tail. Additionally, the surface excess of the partially deuterated C_8AAP was investigated in the absence of PDADMAC. These results provide insights into the molecular order of the surfactants which is also the subject of a manuscript currently under preparation.

Experimental Details

The sample loads required for #9-12-652 were mainly composed from long time measurements resolving structural changes which allowed us to handle the experiment with only two people from our team and the help of *Javier Carrascosa Tejedor, and Philipp Gutfreund.* We are very grateful for their help and advice during the experiment. With the new isotopic contrasts, we were able to complete the data sets recorded in experiment #9-11-1984 by measuring 6 more mixing ratios of C_4AAP/PDADMAC and 9 new mixing ratios of C_8AAP/PDADMAC mixtures.

To address the aims of the experiments we have studied both systems in *3 isotopic contrasts*: h- and d-surfactants in air contrast matched water (ACMW) and d-surfactants in D_2O. Some contrasts of h-surfactants in D_2O could not be performed due to the necessary long time of the structural measurements and the limited number of people executing the experiments. Due to a miscalculation, water with only 0.8 %

D_2O was used instead of ACMW for most of the experiments. For each system, we have kept the surfactant concentration constant at 1 mM C_4AAP or 0.1 mM C_8AAP respective which are close to the maximum changes upon E/Z switching at the air-water interface when there is no polyelectrolyte present. These concentrations can be well justified and are based on our previously published work.[3] For the isotherm of the C_8AAP-surfactant, several concentrations were measured using the deuterated surfactant in ACMW. Even though the isotherm was measured in water initially the isotherm could be remeasured in ACMW.

For experiment #9-12-1984, first the 6-position sample changer adapted to contain both green and UV LEDs (as was done in our previous experiments) was set up. Direct beams and pure solvent calibrations were run for a total of 6 h. After our experiment was done, a misconfiguration of the laser system was detected which affects also our experiment. Therefore, all results had to be carefully re-evaluated.

Data Analysis – Structure of AAP/PDADMAC mixtures at the air-water interface

We conduced structural measurements using the full Q-range for each system. These were done for the C_4AAP/PDADMAC system for polyelectrolyte concentrations of 0.001, 0.004, 0.01, 0.025, 0.1, 0.25, 0.5, 1, and 3 mM while for the C_8AAP/PDADMAC system the concentrations were 0.002, 0.01, 0.02, 0.04, 0.07, 0.1, 0.15, 0.3, and 1 mM. Due to the high number of experiments only a limited number of P/S concentrations can be shown in Figure 2 of this report. Each structural measurement was performed under continuous irradiation and after a sufficient adsorption time (mostly ~90 min). This procedure was repeated for the second irradiation at a different wavelength which leads to two sets of structural data per AAP/PDADMAC mixing ratio. For most experiments, green light was used first and the experiments with UV irradiation were performed afterwards. Only for concentrations close to the expected point of zero net charge, UV light was used first which avoided sedimentation of the aggregates.

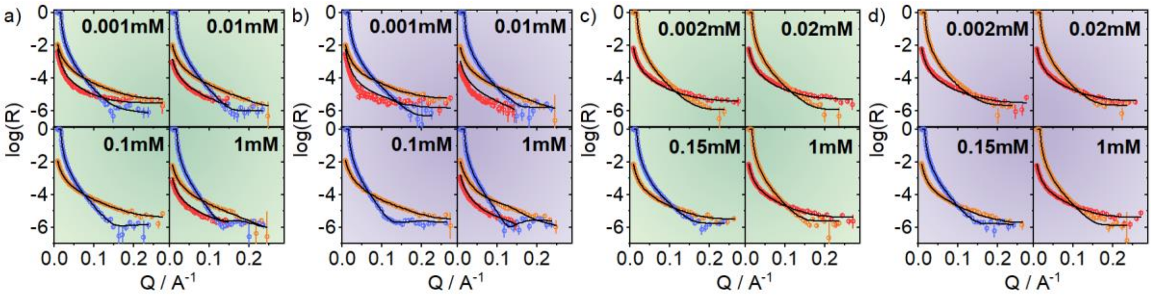

Fig. 2 Exemplary reflectivity profiles for AAP/PDADMAC mixtures in different contrasts for hydrogenous (h-surf) or deuterated (d-surf) surfactants (structures in Fig. 1): h-surf in ACMW (red), d-surf in ACMW (orange) and d-surf in D_2O (blue). Figures present different, selected PDADMAC concentrations and light irradiations (indicated with the background color) as indicated in the figures. Solid, black lines are optimized model fits. Results from our analysis are summarized in Table 1.

The structural data were fitted using a 4-layer model which expands the model of our previous experiment[1], while the analysis is based on the work by STAPLES *et al.*[5]: The chains of the surfactants protrude in the air phase (layer 1), while their heads are still in the solvent phase and interact with the polyelectrolyte (layer 2), which can extend deeper into the solvent phase (layer 3). For some concentrations a small Keissig fringe of the d-surfactant in D_2O is observed which is indicative of extended structures of surfactant hemimicelles (layer 4). In order to keep the number of free parameters low, layer 4 is only applied if the volume fraction of the surfactant exceeds the threshold of 1 %. Some of the fit parameters of the current analysis are shown in Table 1, while the resulting surface excess for all concentrations is presented in Figure 3 below.

Table 1 *Surface excess of AAP surfactant and PDADMAC from the full-Q fits presented in Fig. 2. In addition, structure information of the several layers i.e. the thickness as well the composition (volume fraction Vf) are presented.*

$c_{Poly.}$ / mM	$\Gamma_{surf.}$ / μmolm^{-2}		$\Gamma_{Poly.}$ / μmolm^{-2}		d_1 / Å		d_2 / Å		$Vf_{2,Poly}$ / %		d_3 / Å		$Vf_{3,Poly}$ / %		d_4 / Å		$Vf_{4,surf}$ / %	
C_4AAP/PDADMAC																				
0.001	4.6	4.4	0.9	1.0	16	14	6	6	0	7	8	40	11	2	-	18	-	3.3
0.01	4.6	3.9	1.1	1.6	15	13	4	6	16	24	9	91	0	0.4	-	18	-	1.3
0.1	4.6	4.6	2.1	3.7	16	16	5	4	29	71	137	17	8	8	-	18	-	2.6
1	3.6	4.3	3.5	5.3	12	14	6	6	1	80	7	27	4	4	-	18	-	6.9
C_8AAP/PDADMAC																				
0.002	4.2	3.7	0	0	16	14	4	4	0	0	0	0	0	0	-	-	-	0
0.02	4.0	4.0	0	0.5	15	15	4	4	0	0	0	58	0	1	-	-	-	0
0.15	4.4	4.4	1.1	3.2	17	17	4	4	7	72	45	74	2	1	-	22	-	1.2
1	4.3	4.4	1.7	1.4	16	17	4	4	38	27	66	55	0.6	1	-	-	-	0

From our SFG experiments (not shown) of the mixtures, we conclude that at low PDADMAC concentrations the interfacial charge is negative but decreases to negligible values when the P/S mixing ratio approaches 1. This decrease in the negative net charge is found at relatively lower PDADMAC concentrations. The determined stoichiometry of the C_4AAP/PDADMAC mixtures (Tab. 1, Fig. 3) from NR experiments is indeed consisted with the qualitative conclusions from our SFG experiments: At low concentrations the excess of the anionic surfactant is higher compared to the PDADMAC surface excess. At a P/S ratio of 1 the amount of interfacial PDADMAC and C_4AAP are nearly equal which leads to nearly neutral net charge at the interface. This neutralization of the interfacial charge occurs under UV light at lower concentrations. For the C_8AAP/PDADMAC-mixtures a similar trend is observed.

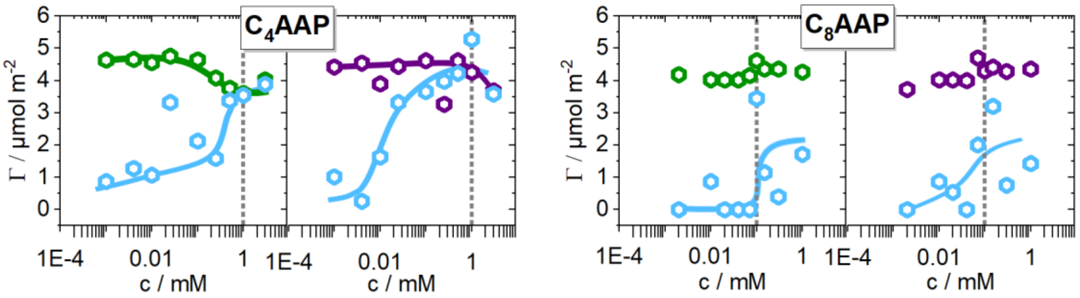

Fig. 3 Calculated surface excess from the preliminary low-Q analysis for the C_nAAP/PDADMAC mixtures as a function of the polyelectrolyte concentration with (left) 1 mM C_4AAP and (right) 0.1 mM C_8AAP as surfactant concentration. The vertical dashed line indicates where the PDADMAC concentration matches the surfactant concertation (P/S ratio = 1).

Data Analysis – Surface excess of C_8AAP solutions

We have recorded NR data in the low-Q range in order to construct the adsorption isotherms for the d_6-C_8AAP system without polyelectrolyte. Each concentration was measured under green and UV irradiation following the recently developed low-Q compositional analysis approach. The C_8AAP surfactant was measured with two different solvents. The results of both experiments were subsequently averaged in order minimize the error of the misconfiguration stated above and to discard possible outliners of the surface excess. These experiments included a kinetic series making use of the high flux at FIGARO after sample loading and/or switching the light irradiation from 90 to 120 min adsorption time dependent on the surfactant concentration.

The results of the NR analysis in Figure 4. The adsorption isotherms under both irradiations show an increase of the surface excess around 0.001 mM C_8AAP. This seems at first to be in conflict with the tensiometry results (not shown) that states a surface activity at higher concentrations according. Here again the combined results from NR and SFG spectroscopy are extremely helpful to capture the interfacial properties in more detail. The amplitude of the aromatic C–H mode from SFG spectroscopy supports the surface activity at low concentrations from NR and gives further insight to the molecular picture: in a direct comparison with the surface excess from NR experiments reveals the C-H amplitude the molecular order of the surfactants. For samples under green irradiation, the SFG amplitude raises steeper with concentration as the surface excess indicating a high molecular order even at low surface coverages. A possible explanation is the formation of surfactant islands at the air-water interface. At higher surface coverages i.e. higher surfactant concentrations a monolayer may be formed which causes the maximum of the SFG amplitude at 0.01 mM. Under UV irradiation the SFG amplitude underestimates the surface excess that indicates a lower orientation of the surfactants.

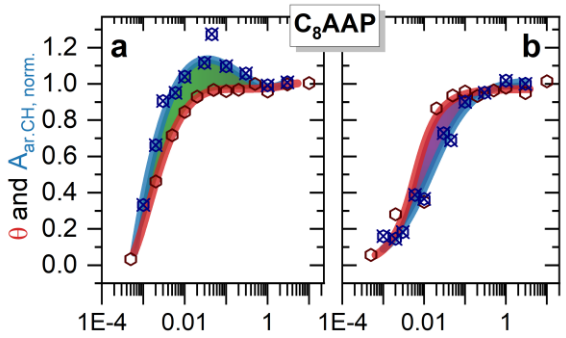

Fig. 4 Calculated surface excess from the low-Q analysis of our NR data for the C_8AAP surfactant without polyelectrolyte compared with the amplitude of the aromatic C–H mode from SFG spectroscopy. Both values are normalized to their last values.

References

1. M. Schnurbus et al. *ACS App. Mat. Int.* **2022***, 14,* 4656. // 2. E. Weißenborn et al. *Chem. Commun.* **2021**, *57*, 5826–5829. // 3. C. Honnigfort et al. *Chem. Sci.* **2020**, *11*, 2085–2092. // 4. N. García Rey et al. *J. Phys. Chem. C* **2019**, *123*, 1279. // 5. E. Staples et al. *Langmuir* **2002**, *18*, 5147.