Smart Air–Water Interfaces with Arylazopyrazole Surfactants and Their Role in Photoresponsive Aqueous Foam

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Supporting Information

ABSTRACT: A new light-switchable azo-surfactant arylazopyrazole tetraethylene glycol carboxylic acid (AAP-E4) was used as a molecular building block to functionalize macroscopic foams. AAP-E4 was studied in the bulk solution with UV/vis spectroscopy and at the interface with sum-frequency generation (SFG) as well as tensiometry. Additional foaming experiments were performed with a dynamic foam analyzer to study the role of AAP-E4 surfactants at the ubiquitous air–water interface as well as within macroscopic foam. In the bulk, it is possible to switch the AAP-E4 surfactant reversibly from trans to cis configurations and vice versa using 380 nm UV and 520 nm green light, respectively. At the interface, we demonstrate the excellent switching ability of AAP-E4 surfactants and a substantial modification of the surface tension. In addition, we show that the response of the interface is strongly influenced by lateral electrostatic interactions, which can be tuned by the charging state of AAP-E4. Consequently, the electrostatic disjoining pressure and thus the foam stability are highly dependent on the bulk pH and the charging state of the interface. For that reason, we have studied both the surface net charge (SFG) and the surface excess (tensiometry) as important parameters that determine foam stability in this system and show that neutral pH conditions lead to the optimal compromise between switching ability, surface excess, and surface charging. Measurements on the foam stability demonstrated that foams under irradiation with green light are more stable than foams irradiated with UV light.

INTRODUCTION

Foams find applications in many industrial processes or as materials from heat insulation to food colloids.1−3 Although foams are lightweight materials with unique properties such as their viscoelastic behavior, most foam properties cannot be changed after completion of the foaming process. Many applications demand high foam stability (FS),4 for example, for surface decontamination, but once this process is completed, it is preferable to switch the foam from stable to unstable conditions enabling easy removal and recycling of the foam constituents. Obviously, there is great interest to turn foams into materials that respond to external stimuli. Although the response of aqueous foam is required on macroscopic length scales, it originates from the ubiquitous air–water interfaces (IFs) as the major building blocks of aqueous foam. For that reason, smart air–water IFs, which are reconfigurable in situ, for various purposes are needed.

As a consequence, it is crucial to change the hydrophobicity and the intermolecular interactions of surface-active molecules with external parameters, such as light,5−9 temperature,1,8 pH,5 magnetic, or electric fields.10,11 The advantage of switching a surfactant with light is that it is easy to manipulate and that the stimulus can be localized both in time and space.12,13 Well-known compounds that change their configurations upon irradiation are derivatives of azobenzene,14,15 stilbene,16,17 and spiropyran.18,19 Azobenzenes are particularly interesting because they switch between trans to cis configurations without any bond breaking. This change in the molecular configuration leads to a significant change in the electronic as well as the steric structure of the surfactant and thus allows for switching its surface activity.

For that reason, adaptive materials attract considerable interest in recent years and photoresponsive IF-controlled materials such as emulsions,20−22 organogels,23 vesicles,24 and microgels25 have been reported. Previous works on light-switchable foams have focused on azobenzene ionic5 and nonionic surfactants. Chevallier et al.26 studied amphiphilic azobenzene derivatives with a cationic head group and described the control of FS and the interfacial properties using light stimuli. In the latter work, the surface tension was higher by irradiation with UV light as compared to blue light conditions. In addition, Chevallier et al. show different foam stabilities in UV light as compared to foams produced in the dark. Lei et al.27 investigated azobenzene surfactants having an anionic head group and also show the switching ability of the surface tension as well of FS for different light conditions. After
irradiation with UV light, the surface tension and the critical micelle concentration increased, whereas the FS decreased. Although previous works have clearly shown that foams and air–water IFs can be made responsive to light and other stimuli, to the best of our knowledge, both the switching kinetics and the reversibility of photoswitching processes at the air–water IF have not been reported so far.

In this article, we study the molecular structure, charging state, and switching kinetics of arylazopyrazole tetraethylene glycol carboxylic acid (AAP-E₄) (Figure 1) as a new light-switchable surfactant for responsive air–water IFs. Arylazopyrazoles are superior analogues of azobenzenes with thermal half-life times superior to most azobenzenes and a smaller switching time compared to most azoles. AAP-E₄ surfactants show unprecedented reversibility of their interfacial molecular structures, which offer unique control on the IF tension and charging state of air–water IFs. To study the latter properties on a molecular level, we have applied both dynamic surface tension measurement and vibrational sum-frequency generation (SFG) and report on in situ measurements, which have been performed during the dynamic change of air–water IFs under light irradiation. In addition, we show the use of the AAP-E₄ surfactant to stabilize macroscopic foam and study the effects of the interfacial molecular structure within macroscopic foam through structure–property relations.

**EXPERIMENTAL DETAILS**

**Sample Preparation.** The synthesis protocol for the arylazopyrazole surfactant is given in brief in the Supporting Information and explained in detail elsewhere.28 All chemicals used for the synthesis (see Supporting Information) of AAP-E₄ surfactants were purchased from Alfa Aesar (Karlsruhe, Germany), Sigma-Aldrich Chemie (Taufkirchen, Germany), or TCI Europe (Zwijndrecht, Belgium) and used without further purification. Solvents were dried before use.

AAP-E₄ solutions were prepared by dissolving the azo-surfactant in ultrapure water (18.2 MΩ cm; total oxidizable carbon ≤3 ppb), which was obtained from a Merck Milli-Q Reference A+ purification system.

The pH was adjusted for all samples (except for the lowest pH) using NaOH (99.99%, Alfa Aesar) dilutions and determined with a pH meter (FiveEasy20, Mettler Toledo). All necessary glassware was precleaned in Alconox solutions (Sigma-Aldrich), and after drying, all parts were soaked in concentrated sulfuric acid with NOCHROMIX (Godax Laboratories) for at least 12 h. Subsequent to the latter treatment, all parts were thoroughly rinsed with ultrapure water. All samples were used immediately after preparation, and the measurements were performed at 295 K room temperature.

**UV/Vis Spectroscopy.** Ultraviolet/visible (UV/vis) absorption spectra were recorded with a PerkinElmer Lambda 650 UV/vis spectrometer in the wavelength region of 250–700 nm. The first spectrum was determined after the sample was irradiated with the green light-emitting diode (LED) for 5 min. After that the sample was irradiated with the UV-LED for 5 min and another spectrum was measured. The same procedure was carried out for the green LED. Irradiation was carried out in four cycles, and the absorbance at the wavelength of 334 nm was recorded as a function of time, additionally.

**Tensiometry.** The surface tension was measured with a pendant drop tensiometer (DSA100, Krüss, Germany) using a modified cuvette. The cuvette was equipped with two long-pass filters (Schott OG590) with a cutoff at 590 nm. This ensures that the light used to determine the drop shape did not affect the arylazopyrazole surfactant. For dynamic surface tension measurements, a drop was formed at the end of a syringe cannula and a charge-coupled device camera monitored its shape for different times after the drop was created. Using image analysis and the Young–Laplace equation, the surface tension was determined from the drop shape as a function of time until equilibrium was reached.30,31

Inside the cuvette, two LEDs with center wavelengths of 385 and 520 nm were placed and used for in situ photoswitching while the dynamic changes in surface tension were simultaneously recorded.

**Vibrational SFG.** SFG is a molecular spectroscopic method based on a second-order nonlinear optical effect.32,33 For SFG spectroscopy, we applied a home-built broadband spectrometer that is described elsewhere.33 At the IF, we overlapped a narrow-band time-asymmetric picosecond beam at 800 nm wavelength [full width at half-maximum (fwhm)] bandwidth <6 cm⁻¹ with a tunable femtosecond infrared (IR) beam which has a broad bandwidth of >200 cm⁻¹ fwhm. In the overlap of both fundamental beams, a third beam was generated with the sum frequency (SF) 0ωFF of the two fundamental frequencies. The intensity of the SF is in this second-order process dependent on the intensities of the two laser beams (IωL and IωIR) and on nonresonant χ(2)NR and resonant parts χ(2)R of the second-order nonlinear susceptibility χ(2) as well as on a third-order contribution which is relevant for charged IFs34–36 with nonzero surface potentials ψ₀

\[
I(ω_{SF}) \propto I_{ω_{L}}^{2} + I_{ω_{IR}}^{2} + \frac{κ}{κ + iΔκ} \mathbf{β} ω_{L}^{2} I_{ω_{IR}}^{2} \psi_{0}^{2}
\]

(1)

In this equation κ is the inverse Debye length and Δκ is the wave vector mismatch between all beams. The resonant part

\[
\chi^{(2)}_{k} = \sum_{i} \frac{A_{i}}{ω_{i} - ω_{IR} + iΔω_{i}}
\]

(2)

is a function of the resonance frequency ω₀ of a molecular vibration, the bandwidth Γ of the vibrational mode k, and the oscillator strength Aᵢ. Here, Aᵢ depends on N the number density of the interfacial molecular species as well as on the orientational average of the Raman polarizability aᵢ and the dynamic dipole moment μᵢ. The dependence on the orientational average of the SF amplitude has a far-reaching consequence for the IF selectivity of the SFG method: for inversion symmetric systems such as bulk liquids and gases, this average is zero for symmetry reason, but IFs such as the air–water IF necessarily break the bulk symmetry and are thus the only source for SFG signals in such systems. For that reason, SFG is inherently IF-specific for an inversion symmetric system where only the few molecular layers at the IF can contribute.

The different contributions provide complementary information: χ(2)k is highly specific for adsorbed molecules because tuning the IR pulse over molecular resonances at the IF leads to resonances in the SFG spectrum. In the case of charged IFs and small, highly polarizable interfacial molecules such as H₂O, the interfacial electric field induces additional polar order and polarization of the latter molecules at the IF. For that reason, the SF intensity of these molecules is also affected

![Figure 1. Molecular structure of AAP-E₄ in both trans and cis conformation.](image-url)
by the interfacial electric field. Because $\chi^{(3)}$ has the same frequency dependence as $\chi^{(1)}$, the amplitude of a vibrational band in SFG spectra can be influenced by $\chi^{(3)}$ effects and is thus dependent on the surface potential which is directly coupled to the surface charge $\sigma_0$ by the Grahame equation.

$$\sigma_0 = \sqrt{8c_e e^2 N_a} \sinh \left( \frac{2c_e e^2 N_a}{2k_B T} \right)$$

(3)

In our experiments, we have recorded SFG spectra in the range of 2800–3800 cm$^{-1}$ by tuning the IR center frequency in seven steps. The acquisition time for each center frequency was 40 s. For a reference, we used a plasma-cleaned polycrystalline gold surface and all sample spectra were normalized to this reference. In addition, we have also recorded in situ spectra while the surfactants were switched from cis to trans configuration. For these measurements, we tuned the IR center frequency again in seven steps but with an acquisition time of 10 s only.

**Foam Characterization.** For the foam characterization, a dynamic foam analyzer (DFA100, Krüss, Germany) was used to determine FS as a function of time. The foam analyzer was placed in an enclosed chamber to avoid unwanted irradiation, for example, from the room lights. The sample solution (70 mL) was filled in a glass column (250 mm length and a diameter of 40 mm) with a porous glass frit (Carl Roth, Germany) which was fixed at the bottom of the column. A nitrogen gas with a flow rate of 0.15 L/min was passed through the glass frit for 50–90 s to produce foams. With the DFA100, it is possible to measure the foam height as a function of foam age by measuring the light transmission through the glass column. For that purpose, an IR LED panel (which does not affect the switching of the surfactant) was installed at one side of the column and on the opposite side, a line sensor was installed. The FS was determined with the bottom of the column. A nitrogen gas with a flow rate of 0.15 L/min was passed through the glass frit for 50–90 s to produce foams. With the DFA100, it is possible to measure the foam height as a function of foam age by measuring the light transmission through the glass column. For that purpose, an IR LED panel (which does not affect the switching of the surfactant) was installed at one side of the column and on the opposite side, a line sensor was installed. The FS was determined with $FS = t/H$, where $H_t$ is the foam height at time $t$ and $H_0$ is the maximum foam height. Prior to foaming, we have irradiated the samples for 15 min with green/UV light inside the foam analyzer enclosure. This procedure initially avoids possible light scattering effects. During foaming and foam aging, irradiation was continued.

**RESULTS AND DISCUSSION**

**UV/Vis Spectroscopy.** Figure 2a presents the UV/vis absorption spectra of 0.1 mM AAP-E$_4$ surfactant dilutions at a solution pH of 7.1. As indicated in the figure, we compare the two spectra of solutions that were recorded after 30 min continuous irradiation with 520 nm green light and 380 nm UV light, respectively. Under green light conditions, we observed a strong absorption band with a maximum centered at the wavelength of 334 nm. A much smaller band is centered at the wavelength of 420 nm and accompanies the band at 334 nm. After exposing the sample with UV light, the absorbance at 334 nm decreased, whereas the absorbance due to a slightly shifted band at 420 nm increases. These substantial changes in the surfactant extinction spectra are indicative for photoisomerization of the arylazopyrazole surfactant from trans (green light) to cis (UV light) configuration (Figure 1).

In Figure 2b we present the absorbance at 334 nm of 0.1 mM AAP-E$_4$ for different cycles of irradiation using UV and green light. Close inspection of Figure 2b shows that the switching process is highly reversible as we did not observe any changes in the peak absorbance between cycles. In Figure 2c, the absorbance at 334 nm is shown as a function of time during which the sample solutions was irradiated with green or with UV light. To obtain quantitative information on the switching kinetics, we have additionally analyzed our UV/vis data in Figures 2c and S1 with respect to apparent rate constants $k$ for which we have assumed first-order kinetics of the light-induced conformational change from trans to cis and vice versa.

Figure 2. (a) UV/vis spectra of 0.1 mM AAP-E$_4$ surfactants in the aqueous solution (pH 7.1) after 5 min irradiation with 520 nm green light and 380 nm UV light as indicated in the figure. (b) Absorbance at 334 nm for four cycles of 5 min irradiation with UV and green light, respectively. (c) Absorbance at 334 nm wavelength as a function of irradiation time with UV (circles) and green light (triangles). The red solid lines in (c) represent fits to the experimental data according to eq 4 (main text).

$$A(t) = A_{eq} \pm (A_0 \mp A_{eq}) e^{-kt}$$

(4)

with $A_{eq}$ and $A_0$ being the absorbance in equilibrium after and before photoswitching, respectively. The photoisomerization was completed within 20 s after the UV light source was switched on. The kinetics of the reverse process (back switch) under green light conditions are much slower and require ~230 s until equilibrium is reached. In Table 1, we present the rate constants $k$ for the switching kinetics from trans to cis conformations in the bulk and at the IF.

| pH     | $k_{trans\rightarrow cis}^{bulk}$ | $k_{cis\rightarrow trans}^{bulk}$ | $k_{trans\rightarrow cis}^{IF}$ | $k_{cis\rightarrow trans}^{IF}$ |
|--------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| pH 4.4 | 20.6                             | 1.7                              | 1.0                              | 0.2                              |
| pH 7.1 | 20.3                             | 1.6                              | 0.7                              | 0.1                              |

Table 1. Rate Constants $k$ for the Switching Kinetics from Trans To Cis Conformations in the Bulk and at the IF.
which are within the limits of the experimental error identical. This observation is consistent with steady-state UV/vis spectra at different pH values, which are independent of pH as well (Figure S1).

**Surface Tension Measurements.** Increasing the pH value causes deprotonation of the AAP-E₄ surfactant carboxylic acid group and consequently leads to a more negatively charged air–water IF. To investigate at which pH conditions the maximum in surface charging is reached, we have recorded both the surface tension and vibrational SFG spectra for different bulk pH values. In Figure 3a, we present the equilibrium surface tension as a function of the bulk pH. Increasing the pH from 4 to 7 leads to an increase in surface tension from 41.7 mN/m to a local maximum in surface tension of 50.1 mN/m. Note that the curves do not overlap because of the superimposed adsorption kinetics.

![Figure 3](image)

*Figure 3. (a) pH dependence of the equilibrium surface tension γ of air–water IFs that were modified by 1 mM AAP-E₄ surfactants. We point out that the ionic strength is changing with the solution pH. Arguments why we have not added a background electrolyte to keep the concentration of AAP-E₄ surfactants was 1 mM for all samples.*

We point out that the differences between the dynamic surface tension with and without light switching are associated with the superimposed adsorption kinetics of the surfactants. The latter are much slower compared to the light-induced changes, and thus, a quantitative comparison of the surface tensions should not be made. We have also studied the photoswitching of the surface tension for different pH values. Although, the reversibility of the interfacial molecular switch (compare Figures 4a vs 4b and S3) and its bulk behavior (Figures 2 and S1) are independent of pH, the switching ability of the IF in terms of changes in the equilibrium surface tension Δγ under different light irradiations did change with the bulk pH and was higher for acidic compared to pH neutral or basic conditions (Figure S3). Partly, this behavior is caused by a lower surface excess at neutral and basic pH values as we will discuss below.

![Figure 4](image)

*Figure 4. (a,b) dynamic surface tensions γ(t) during adsorption and photoswitching at the air–water IF from 1 mM AAP-E₄ surfactant solutions for bulk pH values of 6.9 and 3.9. Data points in green and purple indicate surface tension changes during green and UV light irradiation, respectively. Data points in black color show a reference measurement without photoswitching of the AAP-E₄ surfactant. Note that the curves do not overlap because of the superimposed adsorption kinetics.*

To get quantitative information on the adsorption/desorption rates, we have modeled the dynamic changes in surface tension (Figure 4) using a Gibbs–Langmuir isotherm as a simple model for the adsorption process. This model is chosen because it offers the fewest possible unknown
parameters in our fitting procedures and provides excellent fitting results, as shown in the Supporting Information (Figures S4 and S5). According to the Szyskowski’s equation, we can write for the change in surface tension

\[ \gamma(t) = \gamma_0 \pm RT \Gamma_0 \ln \left( 1 - \frac{\Gamma(t)}{\Gamma_0} \right) \]  

(5)

with \( \gamma_0 \) and \( \Gamma_0 \) as well as \( \gamma(t) \) and

\[ \Gamma(t) = \Gamma_0 \cdot e^{-\frac{t}{\tau}} \]  

(6)

being the surface tension and the surface excess before and during photoswitching with the apparent rate constant \( k_{IF} \) for adsorption or desorption from the air-water IF. For this model, we assume that the conformational change is much faster than the adsorption/desorption kinetics and thus can be neglected compared to the latter. Note that we do not distinguish between two ionic states of AAP-E4 like Boyer et al. as well as Badban and co-workers did for other carboxylic acid surfactants.37,38 For that reason, we report in our study an apparent rate constant, which describes the combined action of both species. The reason why we resort to a simplified model is that it reduces the number of free parameters for fitting the experimental results and enables a comparison of the (overall) kinetics during photoswitching as a function of pH as well as between the IF and the bulk (see below).

In Table 1, we present the results for the rate constants for two different pH values. Comparing the apparent rate constant at pH 3.9 with the rate constant at pH 6.9, we observe a 30% decrease in the rate constant for the photoisomerization from trans to cis, whereas the rate constant from cis to trans decreases by 50%. In addition, a comparison of the absolute values for the rate constants in the bulk with those at the IF shows 20-fold faster kinetics in the bulk. This corroborates our earlier assumption that the kinetics of the photoisomerization can be neglected compared to the interfacial adsorption/desorption kinetics. As we will discuss below, the origin of the different interfacial kinetics is due to the different charging state of the adsorbed AAP-E4 surfactants at the air–water IF.

**Vibrational SFG Spectroscopy.** Figure 5a shows the vibrational SFG spectra that were recorded for 1 mM arylazopyrazole (AAP-E4)-modified air–water IFs at different pH values. The SFG spectra in Figure 5 are dominated by broad bands between 3100 and 3800 cm\(^{-1}\), which can be attributed to O–H stretching vibrations from interfacial water molecules. Two additional but narrow vibrational bands are centered at 2930 and 2980 cm\(^{-1}\) and can be attributed to the CH\(_3\) Fermi resonance and CH\(_3\) antisymmetric stretching vibrations of interfacial arylazopyrazole surfactants, respectively. A much weaker band at 3060 cm\(^{-1}\) is due to aromatic C–H stretching vibrations and is also caused by interfacial arylazopyrazole moieties. All vibrational bands in Figure 5 show dispersive line shapes which are caused by the
interference with a strong nonresonant contribution \( \chi^{(2)}_{NR} \) is also due to the presence of interfacial arylazopyrazole surfactants. Obviously, there are no clear signatures for symmetric methyl stretching vibrations at 2878 cm\(^{-1} \) discernible in our SFG spectra, and only weak contributions from symmetric methylene stretching vibrations at 2850 cm\(^{-1} \) have been observed. The absence of symmetric methyl stretching vibrations is not surprising and is a cause of the molecular structure of the arylazopyrazole surfactant, which has local inversion symmetry at the pyrazole center. The weakness of symmetric methylene stretching vibrations from the tetraethylene glycol E\(_4\) chains is indicative to a significant number of Gauche conformations within the chain which lead to molecular structures with local inversion symmetry and thus negligible SFG signals. This conclusion is corroborated by previous Neutron scattering experiments at air–water IFs that were modified by E\(_4\) ethylene glycol nonionic surfactants.\(^{39}\)

We performed nonlinear least square fits to the pH-dependent SFG spectra of AAP-E\(_4\)-modified air–water IFs in Figures 5a and S7. For that we have assumed model functions for the resonant-effective second-order susceptibility, which we assume as the sum of second-order and third-order contributions (see Vibrational SFG details section). Figure 3b summarizes our fitting results. Here, we present the pH dependence of \( O^−H \) amplitudes from both the low- and high-frequency bands at 3200 and 3450 cm\(^{-1} \), respectively, as well as the pH dependence of the nonresonant contribution \( \chi^{(2)}_{NR} \). With increasing pH value, the latter decreased in amplitude, which was accompanied by an increase in \( O^−H \) amplitudes to the SFG spectra. Because the change in \( \chi^{(2)}_{NR} \) is directly related to the surface excess of AAP-E\(_4\) surfactants,\(^{39}\) we can conclude that the latter decreased with increasing pH. This is consistent with the increase in surface tension as we have discussed above (Figure 3a).

The decrease in surface excess with the solution pH is associated by an increase in surface charging, which we infer from the increase in \( O^−H \) amplitudes.

In Figure 5b, we show the change in SFG spectra while the air–water IF with arylazopyrazole surfactant was irradiated with UV light for 1200 s until equilibrium was reached. Subsequently, the samples were subjected to green light for another 1200 s and a SFG spectrum of the IF was recorded once the IF was in equilibrium. From a close inspection of Figure 5b, it becomes obvious that both the \( O^−H \) intensity and the nonresonant contribution decreased after the sample was irradiated with UV light. The spectrum after subsequent irradiation with green light is within the experimental scatter identical to the spectrum before UV irradiation. This clearly demonstrates the high reversibility of the photoisomerization of the AAP-E\(_4\) surfactant at air–water IFs. However, from the above observations, we can also conclude that the surfactants desorb and readorb to the IF and thus reversibly modulate both the surface charge and the surface excess at the air–water IF as a function of light irradiation and wavelength.

**Foaming Experiments.** To test our conclusions on the interfacial charging state as a function of pH and light conditions, we have performed complementary experiments on the stability of macroscopic foams stabilized by AAP-E\(_4\) surfactants. The FS was measured for different pH values under UV light conditions, see Figure 6a, where the foam height was recorded as a function of time after foaming was completed.

The foam height changes in Figure 6a, clearly show that increasing the pH value leads to more stable foams with a longer lifetime. Foams from pH 7 solutions showed the highest lifetime, whereas a further increase in solution pH leads to a decrease in FS. A comparison of foam stabilities under green light conditions shows comparable changes with pH (Supporting Information). Figure 6b compares the stability at pH 7.1 for green and UV light irradiation. Obviously, the foam that is irradiated with green light showed a much higher stability. At other pH values, we observe the same behavior, but the responsiveness of the foam decreased with increasing pH (see Supporting Information). These results can be compared with the surface tension measurements.

**General Discussion.** Our UV/vis measurements demonstrate that arylazopyrazole AAP-E\(_4\) surfactants can be reversibly photoisomerized from trans to cis configuration. At acidic conditions, the surfactants are less charged but become increasingly charged with increasing pH. SFG spectra and \( O^−H \) amplitudes from air–water IFs indicate that the surface charging of AAP-E\(_4\)-modified air–water interfaces saturates at near to neutral pH conditions. At these conditions, also the surface tension has a local maximum, which is due to a lower surface excess of the arylazopyrazole surfactants. This decrease in surface excess, which is caused by an increase in repulsive electrostatic interactions at the IF, is consistent with the increase in surface tension and the decrease in the nonresonant contribution from AAP-E\(_4\) surfactants to the SFG spectra. This increase in electrostatic interactions causes a decrease in the apparent Gibbs free energy of adsorption \( \Delta G_{eff} \) and thus a decrease in the apparent equilibrium constant. The surface excess \( \Gamma \), as determined from the Gibbs adsorption isotherms at pH 3.8 and 6.9 in Figure S6, is found to be 3.5 \( \mu \text{mol/m}^2 \) (\( \sim 2 \) molecules/nm\(^2 \)) and 2.5 \( \mu \text{mol/m}^2 \) (\( \sim 1.5 \) molecules/nm\(^2 \)) for pH 3.8 and 6.9, respectively. These differences bring strong support to our earlier conclusions of lower apparent equilibrium constants at higher pH. As a consequence, the rate constant for IF adsorption is also decreased. This is corroborated by the differences in IF switching kinetics at pH 3.8 and 6.9 (Table 1). Our data show that the IF with low or negligible net charge at pH 3.8 shows faster switching kinetics as compared to the fully charged IF at pH 6.9 as evidenced by our SFG results (Figures 3b and S). Once all surfactant
molecules at the IF are deprotonated, the interfacial electric field cannot be increased further and an additional increase in solution pH only leads to higher ionic strengths and thus higher screening of the interfacial electric field.

The FS in Figure 6 shows a strong dependence on the interfacial charging state. Obviously, the major stabilization mechanism of the foam with the AAP-E4 surfactants is via the electrostatic disjoining pressure. For that reason, it is not surprising that the highest stability is observed around pH 7. Although at this pH, the surface excess is lower, it provides the maximum surface charging and thus the maximum repulsion forces inside foam lamella. Note that there are other possible foam (de)stabilization mechanisms such as the surface rheology of the surfactant,41 Ostwald ripening, coalescence, steric interactions, and drainage.42 Other factors, such as a different velocity of the surfactant layer and the liquid flow underneath, reported previously by Blanc et al.43 as well as the formation of "caps" in the study on foam films by Mamane et al.44 could also play a role but are beyond the scope of our study while the formation of weak hydrogen bonds between neutral carboxylic acid groups with interfacial water molecules can be ruled out. This is because hydrogen bonding is likely to be stronger between neutral carboxylic acid head groups at a pH close to the head group pK.44,45 Because the foams presented in our study are less stable at pH 3.8—where foam stabilization due to specific hydrogen bonding could play a role—we can conclude that hydrogen bonding is in our case not a relevant factor for the stability AAP-E4 foams (Figure 6).

Once we reduce the electrostatic repulsion forces, for example, by decreasing the pH or by increasing the ionic strength, the FS is substantially reduced. Note that with increasing the pH, the ionic strength also increases, which is the reason why we have not introduced an additional background electrolyte to keep the ionic strength with increasing bulk pH constant. Photocrosslinking of the surfactants from trans to cis configuration at the air–water interface shows that cis isomers at the IF lead to a lower surface excess and surface charging the electrostatic disjoining pressure is reduced and the foam becomes less stable.

CONCLUSIONS

We studied the ability of AAP-E4 to modify the surface tension and the charging state of air–water IFs as a function of external light stimuli using dynamic surface tension measurements and vibrational SFG spectroscopy.

The unique surfactant switching ability and the switching reversibility in the bulk and at the IF was shown as a function of pH and for irradiation with 380 nm UV and 520 nm green light. Results on the behavior of AAP-E4 surfactants at the air–water interface demonstrate that irradiation with UV light causes desorption of molecules from the IF and thus a reduction in surface charging. Green light irradiation changed both the surface tension as well as the surface charging state reversibly back to their initial values before UV light irradiation. Bulk solutions with a pH of ~7 provide the IFs with the highest surface charging, whereas the interfacial electric double layer is only weakly screened by the electrolyte ionic strength.

In addition, we propose that the foams are electrostatically stabilized and thus show the highest FS at pH 7 and a substantial reduction in stability under UV light conditions. This responsiveness of aqueous foam from AAP-E4 dilutions is a direct consequence of their switching ability at air–water IFs. Because the latter are a major building block of aqueous foam, controlling the IF with light-switchable molecular building blocks such as AAP-E4 directly leads to molecular control of macroscopic foam properties via smart air–water IFs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b00587.

UV/vis measurements for pH 7.1 and fitting of the kinetic curves; tensiometry data for different pH values and concentrations; fitting of the tensiometry data; SFG and foam measurements for different pH values; and the synthesis of the AAP-E4 surfactant (PDF)

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Notes

The authors declare no competing financial interest.

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