# Langmuir

# Photofoams: Remote Control of Foam Destabilization by Exposure to Light Using an Azobenzene Surfactant

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**Supporting Information** 

**ABSTRACT:** We report evidence for photocontrolled stability and breakage of aqueous foams made from solutions of a cationic azobenzene-containing surfactant over a wide range of concentrations. Exposure to UV or visible lights results in shape and polarity switches in the surfactant molecule, which in turn affects several properties including critical micelle concentration, equilibrium surface tension, and the air-water interfacial composition (cis isomers are displaced by trans ones). We demonstrate that the trans isomer stabilizes foams, whereas the cis isomer forms unstable foams, a property that does not correlate with effects of light on surface tension, nor with total surfactant concentration. Achieving in situ breakage of foam is accordingly ascribed to the remote control of the dynamics of adsorption/desorption of the surfactant, accompanied by gradients of concentrations out of equilibrium. Photomodulation of adsorption kinetics and/or diffusion dynamics on interfaces is reached here by a noninvasive clean trigger, bringing a new tool for the study of foams.



# ■ INTRODUCTION

Aqueous foams are dispersion of gas bubbles in water, stabilized by amphiphilic molecules adsorbed on the interfaces. Depending on their application, it is required that foams remain stable for long periods of time, even months (e.g., food, cosmetics), or in contrast that bubbles can be rapidly destroyed (e.g., wastewater treatment, flotation to collect minerals). The lifetime of a foam strongly depends on the nature of surfactants present in water. However, on the mechanistic side, the role of surfactants is not easy to identify.<sup>1</sup> Surfactants decrease the energy of bubble formation by decreasing the surface tension, but also provide a protection against the rupture of the thinliquid films between bubbles: steric and electrostatic repulsions between surfactant layers hamper those films to collapse and/or coalesce, and the dynamics of the surfactant play a role in controlling the flow of water in thin films (i.e., foam drainage) caused by gravity. Accordingly, to control foam stability, one should manage with a huge complexity, including adsorption/ desorption dynamics, interfacial resistance to surface flows, interfacial gradients produced by the latter flows, which in turn drives transient fluxes by, for example, Marangoni effect.<sup>1</sup> Breaking foams on demand is thus not easy. In practice, addition of antifoaming agents, especially under the form of emulsions, efficiently triggers irreversible breakage of aqueous thin films.<sup>2</sup> Remote control of foam destabilization by external stimulation has been recently illustrated. In a first case, emulsion was introduced in the aqueous films and light- or temperature-triggered breakage of the stability of the emulsion led to foam destabilization.<sup>3</sup> In a second example, solutions of temperature-responsive surfactants<sup>4</sup> characterized with a transition of the micelles shape from spheres to rods could form temperature-responsive foams. In both cases, the stimuli affect self-assemblies of temperature sensitive amphiphiles in bulk and stability is thus switchable in a narrow range of temperatures (ca. 2–3 °C). To the best of our knowledge, in situ control of foam stability by the direct control of interfacial properties (i.e., in the absence of complex reorganizations occurring in the aqueous film) has never been observed. Simpler systems, such as surfactants whose adsorption/ desorption features are controlled by external stimuli, would help to investigate the relationships between properties of foaming agents.

To this purpose, we propose here a stimuli-responsive surfactant, called photofoamer, that can be switched by a clean external trigger: light. Many stimuli-responsive amphiphilic systems have been popularized recently to manipulate fluids and interfaces by external triggers such as temperature, electric fields, and pH.<sup>5,6</sup> Light-responsive surfactants have been successfully implemented to control phase transition<sup>7,8</sup> or emulsification.<sup>9</sup> None of those responsive amphiphiles were however applied to foams. Photofoamers bring accordingly a promising route to control responses in foams based on simple,

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tractable phenomena. We present here the stability and photodestabilization over a wide range of concentration conditions of foams prepared with an azobenzene-containing molecular surfactant, azoTMA. We show that exposure to light affects also surface tension and the dynamics of surfactant adsorption/desorption, which enables us to propose AzoTMA as a versatile tool to photocontrol surface properties and foamability.

#### DESIGN OF PHOTOFOAMERS

Most amphiphilic molecules imparted to date with sensitivity to light were essentially considered for photoswitching selfassemblies into micelles,<sup>10–12</sup> vesicles,<sup>13</sup> or liquid crystal phases.<sup>14</sup> These molecules contain a photochrome group, and various structures were designed including lipidlike ones,<sup>15</sup> anionic surfactants,<sup>16,17</sup> neutral surfactants,<sup>18,10</sup> or cationic ones.<sup>19</sup> We turned to azobenzene photochromic groups providing rapid and reversible conversions between cis and trans isomers. To amplify the effect of the photoinduced conversion, the variation of molecular shape and aspect parameter was optimized by following Shang et al.:<sup>20</sup> relatively short hydrophobic substituants at 4,4′ positions to achieve large variations of end–end distance upon isomerization (Chart 1).

Chart 1. Structures of Azobenzene-Containing Surfactants and Their Photoinduced Isomerization



The headgroup must accordingly be relatively small to preserve the impact of shape switch. The polar head affects the degree of solubility and foamability. In our hands, cationic surfactants bearing a trimethylammonium polar head brought both high solubility and formed stable foams (Chart 1). We also considered either a neutral headgroup (namely, a short oligoethyleneoxide) or an ionizable one (primary amine, Chart 1), but the latter compounds failed to produce stable foams. Finally, we describe here the trimethylammonium one, AzoTMA, in the following.

# EXPERIMENTAL SECTION

Unless otherwise stated, solutions of AzoTMA, 1 mM to 7 mM (synthesis is described in the Supporting Information), in deionized water were exposed for 30 min under either UV or blue light before use. Under these conditions, the stock solutions reach a photostationnary state containing either a predominant fraction of cis isomer (ca. 96 mol % under UV light) or trans one (ca. 69% under blue light). Details on the measurement of cis:trans ratio are given in the Supporting Information. Light was shone at a maximal power of 0.1

mW (UV light) or 0.4 mW (blue light) from a Prizmatix device equipped with photodiodes (365 or 436 nm), injection system in fibers optics and output collimation optics. The same fiber output was used to irradiate foams at a distance of ca. 1 cm.

Measurements of surface tension were performed on a pendant drop tensiometer (Teclis, France) equipped with an optical device that forms images under red light (long wave pass colored filters with high transmittance above 570 nm) of the surface profiles of aqueous drops hanging in air at the end of a stainless steel capillary. Red light did not affect isomerization of azobenzene. Profiles were matched with Laplace equation to obtain the surface tension. Immediately after formation of the drop, the apparent surface tension decreased, but at times beyond 100 s the rate of decrease slowed down to 0.1 mN·m<sup>-1</sup>·min<sup>-1</sup>. We chose somewhat arbitrarily to record the value of surface tensions at time 100 s. Foams were produced by bubbling air into the column (diameter 1 cm, height 10 cm) containing the solution, at a flow rate of 4 cm<sup>3</sup>·s<sup>-1</sup> for 5 s using a syringe of 0.18 mm diameter. Foam height was measured using image analysis by filming the foam column.

# RESULTS

From solutions of predominantly trans isomers (formed under exposure to blue light, cf. Experimental Section and Supporting Information), we obtained foams that were stable for more than 15 min by flushing air for ca. 5 s in the solution. In contrast, no foam could be maintained for longer than 10 s above solutions containing predominantly cis isomers (solution preirradiated under UV light, cf. Experimental Section). As illustrated in Figure 1, it is possible to modulate the foam stability without any stimulation by simply preparing mixtures of cis-rich and trans-rich solutions in various proportions.

For applied purposes, however, in situ responses to light open more interesting perspectives. In Figure 2, we show that exposure to UV light that was switched on after the formation of trans-rich foam rapidly destabilizes the column of bubbles. When UV light is applied on the top of the foam (here from a Prizmatix's UV led), rapid breakage occurs and all the bubbles have vanished after a few seconds. This photoresponse was achieved over a wide range of concentrations, either below and above the CMC (2 mM) of the blue-adapted AzoTMA. This makes AzoTMA a promising tool for remote control of foams. Note that after shining blue light for several minutes on the solution obtained from the broken foam it is possible to make stable foams again.

Several interfacial properties are made responsive to cistrans isomerization. In Figure 3, curves of equilibrium surface tension isotherms clearly indicate that, below 1 mM AzoTMA, the surface tension of the cis-rich solution is typically higher than that of trans-rich one. The plateau of the surface tension, where the interface is saturated with surfactants and where micelles are expected to form in the bulk, is also clearly shifted to higher concentration upon exposure to UV. It is not surprising that the apolar trans AzoTMA is more surface active and more prone to assemblies than its cis isomer.<sup>21,22</sup> Compared to other examples of azo- surfactants studied to date, the present one reaches however one of the highest amplitude of photoswitch of surface tension (c.a. 20 mN·m<sup>-1</sup> increase under exposure to UV of solutions of all-trans isomers, which compares favorably with the maximum of 14.5 mN·m<sup>-1</sup> reached previously).<sup>20,23</sup>

High variation of surface tension reflects markedly different adsorption properties of cis and trans isomers and typically a lower equilibrium density of cis azoTMA on the air—water interface. However, surprisingly, the photocontrol of foams was achieved irrespective of the total surfactant concentration even



Figure 1. Foam height formed after bubbling 20 mL of air in mixtures of cis and trans azoTMA (1.1 mM) under red light (mol % of cis isomer is quoted in figure). Top: photographs of samples after 25 s incubation in the dark. Bottom: height of the foam columns as a function of incubation time. Mixtures of cis and trans isomers in various proportions were prepared by mixing aliquots of a cis-rich (UV-adapted) and a trans-rich (blue adapted) stock solutions (cf. Experimental Section).



**Figure 2.** Destabilization of foam by exposure to light. Foams were prepared by bubbling air in aqueous solutions of azoTMA at concentrations quoted in the figure. At time zero, the air flush was stopped and samples were either kept in the dark (concentration 1.1 mM, open diamonds) or exposed from the top to UV (surfactant concentration 1.1 mM full squares, 2.3 mM full triangles, 7 mM full circles) or infrared light (1.1 mM full diamonds). The intensity of the IR illumination was chosen to obtain the same local heating of water as with UV. There is no significant destabilization of the foam under such IR conditions.



**Figure 3.** Surface tension of azoTMA cis:trans mixtures measured after 100 seconds by pendant drop method without light stimulation as a function of total surfactant concentration. Squares: predominantly trans azoTAB, i.e. solution exposed to blue light  $(436 \pm 10 \text{ nm})$  prior to measurements containing 69% of trans isomers. Circles: solutions exposed to UV light  $(365 \pm 10 \text{ nm})$  prior to measurements and containing 4% of trans isomers. Inset shows the same data plotted as a function of the concentration of trans-azoTMA. The rescaling of the data shows that the equilibrium surface tension is controlled by the trans concentration.

on the surface tension plateau above 5 mM. For instance, photobreakage persisted at 7 mM azoTMA, although the equilibrium surface tensions of both stationary states differ by less than 2 mN·m<sup>-1</sup>. A similar question was raised by Shin and colleagues<sup>21,24</sup> to interpret light-triggered detachment of pendant drops in systems displaying photovariations of surface tension by less than 2 mN·m<sup>-1</sup>. In the following, we focus on the mechanism of foam destabilization under UV light.

As shown in the inset of Figure 3, the two isotherms can be rescaled on a single master curve by normalization to the concentration of trans AzoTMA instead of the total surfactant concentration. This rescaling betrays that surface tension is mainly controlled by the concentration in trans AzoTMA and that at long times, the interface is mainly covered by trans isomers, even for cis-rich solutions.

In a previous theoretical work<sup>25</sup> focusing on the adsorption/ desorption kinetics of the same AzoTMA system at a simple air—water interface, we showed that the desorption constant of the cis isomer is 2 orders of magnitude higher than that of the trans isomers. Therefore, when UV light is shone on a transrich interface, the adsorbed trans isomers convert into cis isomers that rapidly desorb from the interface, in a few seconds (Figure 4). Above a critical light intensity, the cis—trans switching at the interface can thus become faster than the trans adsorption. As a result, the total number of adsorbed surfactants is expected to decrease with time and light intensity.

This desorption shall occur irrespective of the concentration in bulk being above or below CMC. The interfacial desorption of the cis-isomers could accordingly explain the destabilization of the foam: first, the protection of thin-liquid films against coalescence is likely weakened upon desorption of a significant fraction of the surfactant. Second, one could argue that such desorption may cause a modification of the surface elasticity or viscosity, which are known to play a strong role on foam stability.<sup>1</sup> Indeed Yim and Fuller<sup>26</sup> found that Langmuir monolayers of nonsoluble cis and trans azosurfactants have different surface elasticities because the trans isomers form well organized layers through  $\pi$ -stacking of azobenzene rings. The



**Figure 4.** Schematic drawing of the phototriggered adsorption/ desorption exchanges between subphase and interface under light stimulation. Without stimulation, the interface of a solution prepared either under UV light or blue light prior to measurement is mostly covered with trans isomers. When UV light is shone on the sample, the adsorbed trans-isomers convert into their cis form that rapidly desorbs from the interface. Note that this desorption process occurs whatever the initial cis—trans composition of the bulk solution, i.e., for solutions prepared under UV or blue light. In the case where UV light is shone on a UV-adapted solution, the composition of the bulk solution does not change with time.

surface rheological measurements (both shear and dilational) that we performed showed a weak and non-monotonous variation with the surfactant concentration that could not account for our results. Third, we have to consider that hydrodynamical flows will presumably be created in the films because light intensities shone on the various liquid interfaces in the foam are not homogeneously distributed and depend on orientations of films, and position in the sample. Non-homogeneous exposure would result in gradients of surface tension that are expected to drive, for example, Marangoni flows. Hydrodynamical flows are known to be involved in foam stability, and this point will deserve further investigations out of the scope of the present work.

### CONCLUSION

AzoTMA is a promising tool, tailored to achieve photoswitchable control of the stability of foams and of interfacial properties. Several parameters that are known to be relevant in foam stability are effectively affected by exposure to light, including equilibrium surface tension, CMC, and dynamic competition between adsorption and desorption of surfactant. Because cis AzoTMA is essentially excluded from the interface by the trans isomer, the photostationnary state (eventually reached in bulk) cannot be reached on the irradiated interface. Light accordingly maintains a flux of desorption of cis form, that is, a state out of equilibrium. This effect is expected to drive flows of molecules at interfaces and in the bulk solution, likely to play a role in foam destabilization. Interfacial properties of AzoTAB bring an interesting new toolbox to investigate the complexity of mechanisms of foam destabilization. Control of foam stability uses 90% of the surfactants produced in the world (e.g., in applications such as flotation), which is environmentally harmful. Better understanding of breakage of foams and reusable surfactants in this context would save enormous quantities of polluting agents.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Synthesis of azosurfactants; determination of cis:trans ratios by <sup>1</sup>H NMR and UV spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Langevin, D. ChemPhysChem 2010, 9, 510-522.
- (2) Denkov, N. D. Langmuir 2004, 20, 9463-9505.
- (3) Salonen, A.; Langevin, D.; Perrin, P. Soft Matter 2010, 6, 5308-5311.
- (4) Fameau, A. L.; Saint-Jalmes, A.; Cousin, F.; Hoinsou-Housou, B.; Novalles, B.; Nallet, F.; Gaillard, C.; Boué, F.; Doulliez, J.-P. Angew. Chem., Int. Ed. 2011, 50, 8264–8269.
- (5) Liu, X. Y.; Abbott, N. L. J. Colloid Interface Sci. 2009, 339, 1–18.
  (6) Rosslee, C.; Abbott, N. L. Curr. Opin. Colloid Interface Sci. 2000,
- 5, 81–87.
- (7) Eastoe, J.; Vesperinas, A. Soft Matter 2005, 1, 338-347.
- (8) Eastoe, J.; Wyatt, P.; Sanchez-Dominguez, M.; Vesperinas, A.;
- Paul, A.; Heenan, R. K.; Grillo, I. *Chem. Commun.* **2005**, 2785–2786. (9) Khoukh, S.; Perrin, P.; Bes de Berc, F.; Tribet, C. *ChemPhysChem* **2005**, 6, 2009–2012.
- (10) Lee, C. T.; Smith, K. A.; Hatton, T. A. Langmuir 2009, 25, 13784–13794.
- (11) Shang, T. G.; Smith, K. A.; Hatton, T. A. Langmuir 2006, 22, 1436–1442.
- (12) Bonini, M.; Berti, D.; Di Meglio, J. M.; Almgren, M.; Teixeira, J.; Baglioni, P. *Soft Matter* **2005**, *1*, 444–454.
- (13) Liu, Y.-C.; Ny, A.-L. M. L.; Schmidt, J.; Talmon, Y.; Chmelka, B. F.; C. Ted Lee, J. *Langmuir* **2009**, *25*, 5713–5724.
- (14) Minkenberg, C. B.; Florusse, L.; Eelkema, R.; Koper, G. J. M.; van Esch, J. H. J. Am. Chem. Soc. **2009**, 131, 11274.
- (15) Song, X. D.; Perlstein, J.; Whitten, D. G. J. Am. Chem. Soc. 1997, 119, 9144–9159.
- (16) Lin, Y. Y.; Cheng, X. H.; Qiao, Y.; Yu, C. L.; Li, Z. B.; Yan, Y.; Huang, J. B. Soft Matter **2011**, *6*, 902–908.
- (17) Eastoe, J.; Zou, A.; Espidel, Y.; Glatter, O.; Grillo, I. Soft Matter 2008, 4, 1215–1218.
- (18) Yang, L.; Takisawa, N.; Hayashita, T.; Shirahama, K. J. Phys. Chem. **1995**, *99*, 8799–8803.
- (19) Matsumura, A.; Tsuchiya, K.; Torigoe, K.; Sakai, K.; Sakai, H.; Abe, M. *Langmuir* **2011**, *27*, 1610–1617.
- (20) Shang, T. G.; Smith, K. A.; Hatton, T. A. Langmuir 2003, 19, 10764–10773.
- (21) Cicciarelli, B. A.; Hatton, T. A.; Smith, K. A. *Langmuir* **2007**, *23*, 4753–4764.
- (22) Lee, C. T.; Smith, K. A.; Hatton, T. A. Langmuir 2009, 25, 13784–13794.
- (23) Diguet, A.; Guillermic, R. R.; Magone, N.; Saint-Jalmes, A.;
- Chen, Y.; Yoshikawa, K.; Baigl, D. Angew. Chem., Int. Ed. 2009, 48, 928. (24) Shin, J. Y.; Abbott, N. L. Langmuir 1999, 15, 4404-4410.
- (25) Chevallier, E.; Mamane, A.; Stone, H. A.; Tribet, C.; Lequeux,
- F.; Monteux, C. Soft Matter 2011, 7, 7866–7874.

(26) Yim, K. S.; Fuller, G. G. Phys. Rev. E 2003, 67, 041601.