

# Using Light to Control Dynamic Surface Tensions of Aqueous Solutions of Water Soluble Surfactants

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We report the use of UV light to control the dynamic surface tensions of mixed surfactant systems containing sodium dodecyl sulfate, SDS, and 4,4'-bis(trimethylammoniumhexyloxy)azobenzene bromide, BTHA. The light influences the dynamic surface tension of these solutions by driving the isomerization of the azobenzene moiety from *cis* to *trans*. By combining use of the du Nouy ring, maximum bubble pressure, and Wilhelmy plate methods to measure dynamic and equilibrium surface tensions, the dynamic surface tension of an illuminated aqueous solution of these surfactants is demonstrated to be up to 25 mN/m lower than the dynamic surface tension of a solution not previously exposed to UV light. In contrast, the equilibrium surface tensions of these solutions change by less than 2 mN/m upon illumination. Measurements of quasi-elastic and static light scattering from these mixed surfactant solutions support our hypothesis that illumination influences the dynamic surface tension through its effect on the state of aggregation of the surfactant in bulk solution and thus the rate of mass transport of surfactant to the surface of the solution. A decrease in the number density of aggregates in solution upon illumination is observed. The decrease in dynamic surface tension that follows illumination is used to trigger the release of droplets of aqueous solution from a capillary at specified times. Patterned illumination is used to select the release of droplets from an array of droplets.

## Introduction

We report the use of light and a light-sensitive, water soluble surfactant to trigger changes in the dynamic surface tensions of aqueous solutions of surfactants. Whereas the properties of classical surfactant systems are largely fixed by the concentrations of surfactant and electrolyte dissolved within a solution,<sup>1</sup> photosensitive surfactants offer the possibility of both spatial and temporal control of the properties of surfactant-based systems by application of light. The capability to use light to control properties such as surface tension and phenomena such as the spreading of liquids and solubilization of solutes can provide new principles for the manipulation of liquids suitable for use, for example, during coating processes<sup>2</sup> as well as for use in microfluidic and micro-analytical devices.<sup>3</sup> Because surface tensions of surfactant solutions typically take minutes or hours to reach their equilibrium values whereas many useful fluid phenomena (e.g., spreading) occur on time scales of seconds or less, in this paper we focus on the development of principles for active control of *dynamic* surface tensions of surfactant solutions using light.

Two past studies have reported principles for active control of interfacial properties of surfactant systems. First, electrochemical control of the oxidation state of the ferrocenyl moiety within the redox-active surfactant  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{11}\text{Fc}$ , where Fc is ferrocene, was shown to drive changes in surface tensions of aqueous solutions as large as 23 mN/m.<sup>4-9</sup> Reversibility was demonstrated by repeatedly oxidizing and reducing the surfactant, thus

causing the surface tension to cycle between high and low values of 72 and 49 mN/m, respectively. Spatially localized reduction of  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{11}\text{Fc}^+$  to  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{11}\text{Fc}$  at the air/water interface was also demonstrated to produce gradients in surface tension and thereby cause fluid motion (Marangoni phenomena).<sup>6</sup> The speed and direction of the Marangoni flow was controlled by using two working electrodes and by creating surface-active species ( $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{11}\text{Fc}$ ) at one electrode and consuming them at the other electrode. A second set of past studies has reported principles for active control of interfacial properties of surfactant solutions by using redox-active surfactants containing disulfide bonds,  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_8\text{SS}(\text{CH}_2)_8\text{N}^+(\text{CH}_3)_3$ .<sup>10</sup> Whereas reduction of a 1 mM solution of  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_8\text{SS}(\text{CH}_2)_8\text{N}^+(\text{CH}_3)_3$  to  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_8\text{SH}$  by addition of a chemical reducing agent (e.g., dithiothreitol) was reported to cause the surface tension of an aqueous solution to increase from 58 to 72 mN/m, the surface tension measured *during* the transformation decreased to values as low as 48 mN/m. The reaction-induced lowering of surface tension resulted from a transient accumulation of  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_8\text{SH}$  at the surface of the solution. The transient accumulation of  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_8\text{SH}$  was caused by its slow rate of desorption as compared to its rate of formation from the disulfide. While these past studies demonstrate the potential usefulness of redox-active surfactants for active control of surfactant solutions, they also point to some limitations of electrochemical approaches. First, the use of electro-

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(1) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1989.

(2) Zhang, X. G.; Basaran O. A. *J. Colloid Interface Sci.* **1997**, *187*, 166.

(3) Delamarche, E.; Bernard, A.; Schmid, H.; Michel, B.; Biebuyck, H. *Science* **1997**, *276* (5313), 779.

(4) Gallardo, B. S.; Abbott, N. L. *Langmuir* **1997**, *13* (2), 203.

(5) Gallardo, B. S.; Metcalfe, K. L.; Abbott, N. L. *Langmuir* **1996**, *12* (17), 4116.

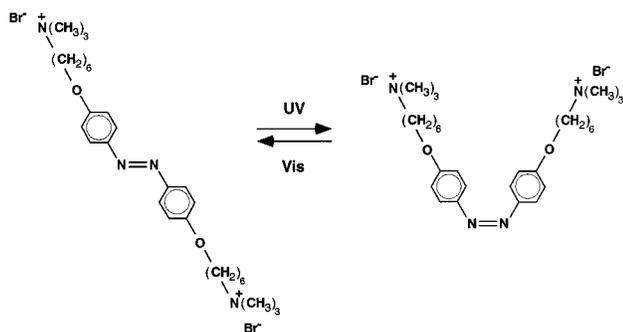
(6) Bennett, D. E.; Gallardo, B. S.; Abbott, N. L. *J. Am. Chem. Soc.* **1996**, *118* (27), 6499.

(7) Gallardo, B. S.; Hwa, M. J.; Abbott, N. L. *Langmuir* **1995**, *11* (11), 4209.

(8) Aydogan, N.; Gallardo, B. S.; Abbott, N. L. *Langmuir* **1999**, *15* (3), 722.

(9) Gallardo, B. S.; Gupta, V. K.; Eagerton, F. D.; Jong, L. I.; Craig, V. S.; Shah, R. R.; Abbott, N. L. *Science* **1999**, *283*, 57.

(10) Jong, L. I.; Abbott, N. L. *Langmuir* **1998**, *14*, 2235.



**Figure 1.** Molecular structure of the light-sensitive surfactant BTHA shown in *trans* and *cis* states.

chemical methods to control the oxidation state of redox-active systems requires that electrodes be inserted into the system: the necessary presence of the electrodes constrains the possible range of experimental setups. For example, in some cases, electrodes can pin the motion of three-phase contact lines. Second, because rates of oxidation and reduction during electrochemical transformations are limited by rates of transport of surfactants to and from electrodes, it is difficult to drive changes in surfactant-based properties of solutions with diffusion lengths greater than  $\sim 10 \mu\text{m}$  over times shorter than a few seconds.

In this paper we report an investigation of an alternative approach to the development of principles for active control of surfactant systems that does not rely on redox transformations. This approach uses light to trigger changes in surfactant-based properties of solutions. The rate of the response of these systems is, in principle, limited only by rates of light-driven transformations, which can occur on time scales of nanoseconds,<sup>11</sup> and the characteristic relaxation times of surfactant solutions. In addition, straightforward experimental procedures exist to pattern light on materials as a function of both position and time. We aim to exploit these procedures to achieve spatial and temporal control of surfactant-based properties of solutions.

The light-sensitive surfactant we report here is based on the azobenzene moiety (Figure 1). Azobenzene is photoactive and assumes one of two isomeric states (*cis* or *trans*) depending upon the wavelength of light used to illuminate the compound.<sup>12</sup> The *trans* isomer absorbs UV light with a wavelength of 360 nm and, upon illumination, is transformed into the *cis* isomer. Because the *cis* isomer absorbs light with a wavelength of 460 nm, illumination of the *cis* state with visible light causes the *cis* isomer to relax back to the *trans* isomer. Because the absorption peaks of the two isomers overlap, however, complete conversion to the *cis* or *trans* isomer cannot generally be accomplished.<sup>13</sup> Instead, upon illumination, these systems typically reach photostationary states comprised of a mixed population of *trans* and *cis* isomers, the composition of which is a function of the wavelength of light used to illuminate the system. Past studies have demonstrated that isomerization of azobenzene-containing molecules can be used to induce isothermal phase changes in thermotropic and lyotropic liquid crystalline systems.<sup>14,15</sup> Langmuir–Blodgett films of water insoluble amphiphiles containing azobenzene have also been used as “command

layers” to direct the anchoring of liquid crystals<sup>16</sup> and to control wetting behavior.<sup>17</sup> In contrast to these past studies, our research focuses on control of interfacial properties by using *water soluble* surfactants that contain azobenzene. Hayashita and co-workers<sup>18,19</sup> have examined how UV light affects the state of aggregation and surface tension of solutions of the water soluble surfactant  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_2\text{OAzCH}_2\text{CH}_3$ , where Az is the azobenzene moiety. Aqueous solutions of this surfactant measured after illumination had slightly higher critical micellar concentrations (12 mM) as compared to those prior to illumination (10 mM). The largest change in surface tension upon illumination with UV light was reported to be  $\sim 4 \text{ mN/m}$ . Although these past studies demonstrate control of surface tensions of surfactant systems by using light, the magnitudes of the changes reported are too small to be useful. In this paper, we report an azobenzene-based surfactant and procedures that make possible large changes ( $\sim 25 \text{ mN/m}$ ) in interfacial properties of aqueous systems by using light.

The approach we have pursued to achieve active control of dynamic surface tensions of surfactant solutions uses light to change the extent of aggregation of surfactants within bulk solution. Past studies have established that the diffusion coefficients of aggregates of surfactants with hydrodynamic diameters of  $\sim 150 \text{ nm}$  (e.g., vesicles) are  $\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  whereas diffusion coefficients of monomeric surfactants are  $\sim 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .<sup>20</sup> By estimating the characteristic time for surfactant molecules to diffuse to a freshly formed interface,  $t_D$ , as

$$t_D \sim \frac{\Gamma^2}{c^2 D} \quad (1)$$

where  $\Gamma$  is the excess surface concentration of surfactant at equilibrium,  $c$  is the bulk concentration of surfactant, and  $D$  is the effective diffusion coefficient of the surfactant in the bulk solution, we calculate that the disassembly of large aggregates into monomers in solution can change  $t_D$  by up to 2 orders of magnitude. This result suggests that light-induced changes in the state of aggregation of surfactants in solution may lead to large changes in dynamic surface tensions through their effect on the mass transport of surfactant to the surfaces of solutions. We also note that light-induced changes in micellar relaxation times could further change rates of transfer of surfactant from aggregates to the surfaces of surfactant solutions, thus creating an additional mechanism by which isomerization could affect dynamic surface tension.<sup>21,22</sup>

The experimental approach reported in this paper is based on two strategies that we predicted would lead to surfactant systems capable of undergoing large changes in their states of aggregation upon photoisomerization. First, we designed and synthesized a bolaform surfactant containing azobenzene. Bolaform surfactants, which have the structure  $\text{R}(\text{CH}_2)_n\text{R}$ , where R is a polar group, assume conformations within aggregates that are more constrained as compared to those of surfactants with one

(16) Sekkat, Z.; Buchel, M.; Orendi, H.; Knobloch, H.; Seki, T.; Ito, S.; Koberstein, J.; Knoll, W. *Opt. Commun.* **1994**, *111*, 324.

(17) Moller, G.; Harke, M.; Motschmann, H. *Langmuir* **1998**, *14*, 4955.

(18) Hayashita, T.; Kurosawa, T.; Miyata, T.; Tanaka, K.; Igawa, M. *Colloid Polym. Sci.* **1994**, *272*, 1611.

(19) Yang, L.; Takisawa, N.; Hayashita, T.; Shirahama, K. *J. Phys. Chem.* **1995**, *99*, 8799.

(20) Chang, C.; Franses, E. *Colloid Surf., A* **1995**, *100*, 1.

(21) Patel, S. S.; Kumar, K.; Shah, D. O.; Delfino, J. J. *J. Colloid Interface Sci.* **1996**, *183*, 603.

(22) Aniansson, G. E. A. *Prog. Colloid Polym. Sci.* **1985**, *70*, 2.

(11) Ikeda, T.; Osamu, T. *Science* **1995**, *268*, 1873.

(12) The *trans* isomer is thermodynamically stable whereas the *cis* isomer undergoes a first-order thermal isomerization to the *trans* state.

(13) Fisher, E.; Frankel, M.; Wolovsky, R. *J. Chem. Phys.* **1955**, 1367.

(14) Legge, C. H.; Mitchell, G. R. *J. Phys. D* **1992**, *25*, 492.

(15) Wolff, T.; Klaubner, B.; von Bunau, G. *Prog. Colloid Polym. Sci.* **1990**, *83*, 176.

polar R group because both R groups of the bolaform surfactant maintain contact with the aqueous phase when the surfactant is assembled within aggregates in bulk solution or at the surface of a solution.<sup>23</sup> Photoisomerization of bolaform surfactants would, we predicted, lead to large changes in aggregation as compared to those for single-headed surfactants. Second, we based our studies on a mixed surfactant system containing anionic and cationic surfactants because the headgroup areas occupied, on average, by molecules within aggregates formed by anionic and cationic surfactants are small as compared to those for systems formed from single-component ionic surfactants. For example, surfactant molecules hosted within vesicles formed from mixtures of cetyltrimethylammonium bromide and sodium octyl sulfate occupy areas as small as 36 Å<sup>2</sup>/molecule.<sup>24</sup> The close packing of surfactant molecules within monolayers or bilayers formed from surfactants of opposite charge should, therefore, increase steric interactions between molecules and thus amplify the effects of photoisomerization on the structure and properties of these solutions. In this paper, we report the properties of solutions formed from mixtures of 4,4'-bis(trimethylammoniumhexyloxy)azobenzene bromide, BTHA (a bolaform surfactant with cationic headgroups, Figure 1), and sodium dodecyl sulfate, SDS (an anionic surfactant).

We used the du Nouy ring<sup>25</sup> and maximum bubble pressure<sup>26</sup> (MBP) methods to measure dynamic surface tensions of aqueous solutions of BTHA and SDS. The du Nouy ring method is based on a Pt/Ir ring that is immersed beneath the surface of the surfactant solution and then pulled upward to form a cylindrical film of liquid. The ring rises and extends the interface until a maximum force is measured. In our experiments, the maximum force was reached within 10–15 s from the time at which the ring began to extend the surface area of the solution. The maximum bubble pressure method is based on measurements of the pressure difference across the surface of a bubble produced at the tip of a capillary. The pressure difference is related to the surface tension by the Laplace equation. In practice, a pressure differential is measured between two capillaries of different size so as to eliminate the effects of hydrostatic pressure. The rate of bubbling can be changed from ~0.1 to ~100 Hz<sup>26</sup> so as to examine the dynamic surface tension over time scales of a few milliseconds to many seconds. We formed bubbles at the tip of the orifice with a frequency of ~0.1 Hz.

While both the du Nouy ring and MBP methods provide measurements of dynamic surface tensions, the effective "ages" of the surfaces characterized by these two methods are different. The du Nouy ring method involves a small extension of a pre-existing surface (with an age of minutes) over an interval of time of ~10 s. The effective "age" of the surface characterized by this method reflects the age of the pre-existing surface as well as the interval of time over which the surface is extended. In contrast, when using the MBP method, an entirely new surface is created with each bubble. The surface tension is measured during the growth of the bubble and at the instant the pressure in the capillary reaches its maximum. The effective age of the surface characterized by this method is substantially less than the interval of time between the formation of bubbles for two reasons. First, this method characterizes the state of an expanding surface and thus the effective

age of the surface is less than that of a nondeforming interface. Second, after the growth and release of the bubble, the surface retracts into the capillary and must be expelled prior to the growth of the next bubble.<sup>27</sup> We conclude that our measurements using the MBP characterize surfaces of solutions that have effective ages that are less than that characterized when using the du Nouy ring.

Whereas the du Nouy and MBP methods were used for measurements of the dynamic surface tensions, we used the Wilhelmy plate method<sup>28</sup> to measure equilibrium surface tensions of solutions of BTHA and SDS. In this method, the surface tension of a stationary interface is measured using a Pt plate. For solutions that completely wet the Pt surface, the force on the plate is equal to the product of the length of the perimeter of the plate and the surface tension.

## Experimental Section

**Synthesis.** All reagents were obtained from Aldrich (Milwaukee, WI). The surfactant BTHA was synthesized by using the following scheme. First, the 4,4'-dihydroxyazobenzene was prepared according to the literature.<sup>29</sup> Briefly, 4-aminophenol (5.45 g) was combined with concentrated hydrochloric acid (20 mL) and water (80 mL) and cooled to 0 °C in a salt water/ice bath. Sodium nitrite (3.5 g) dissolved in water (300 mL) was slowly added to this solution over 2.5 h. The temperature of the solution was maintained below 3 °C during the addition. The resulting purple diazonium solution was then added to an aqueous slurry containing copper sulfate pentahydrate (22.3 g), water (50 mL), ammonium hydroxide (30% v/v, 15 mL), and hydroxylamine hydrochloride (3.5 g) over 5 min. The solution was stirred for 1 h with additions of ethyl ether to reduce foaming. The precipitates were filtered, washed with dilute HCl and water, and dried. The brown solid was recrystallized in ethanol/water to produce red crystals (2.51 g, 47% yield).

The dihydroxyazobenzene dissolved in ethanol was alkylated by addition to a refluxing ethanolic solution of potassium hydroxide (2.5 eq) and 1,6-dibromohexane (10 eq) over 4 h. The resulting solid was quaternized in ethanol with trimethylamine for 5 days at 55 °C to form BTHA. The yellow product was recrystallized three times in ethanol to obtain the final product. The structure was confirmed by <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ/ppm = 1.34 (q, 4H, CH<sub>2</sub>), 1.49 (q, 4H, CH<sub>2</sub>), 1.75 (m, 8H, CH<sub>2</sub>), 2.49 (s, solvent), 3.05 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>N), 3.34 (m, water and NCH<sub>2</sub>), 4.07 (t, 8H, CH<sub>2</sub>O), 7.11 (d, 4H, H<sub>aromatic</sub>), 7.83 (d, 4H, H<sub>aromatic</sub>) and elemental analysis (C<sub>30</sub>H<sub>50</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>2</sub> with 1.4 equiv of H<sub>2</sub>O. Calc: C, 52.70; H, 7.78; N, 8.19; O, 7.96; Br, 23.37; C/N, 6.43; C/Br, 2.25. Found: C, 52.78; H, 8.06; N, 8.26; O, 8.05; Br, 24.62; C/N, 6.39; C/Br, 2.14).

**Physical Measurements.** All measurements of surface tension were performed at 25 °C. Solutions were prepared using Milli-Q water (18.2 MΩ cm, Millipore) and NaCl that was recrystallized from Milli-Q water and then dried at 350 °C overnight. The SDS was recrystallized in ethanol three times before use. All glassware was cleaned in piranha solution (concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub>, 70/30) before use. **Warning:** Piranha solution should be handled with extreme caution; in some circumstances (probably when it has contacted significant quantities of an oxidizable organic material), it has detonated unexpectedly.

Aqueous solutions of BTHA and SDS were illuminated using a HgXe arc lamp (Oriel, Stratford, CT, lamp 6137, power supply 8500) or a pen lamp with a filter (Oriel, lamp 6035, power supply 6047, filter 6042). The extent of isomerization of BTHA was determined from measurements of the UV–vis absorption spectra of aqueous solutions.<sup>19</sup>

(23) Diamant, H.; Andelman, D. *Langmuir* **1994**, *10*, 2910.

(24) Yuet, P. K.; Blankstein, D. *Langmuir* **1996**, *12*, 3802.

(25) Harkins, W. D.; Jordan, H. F. *J. Am. Chem. Soc.* **1930**, *52*, 1751.

(26) Fainerman, V. B.; Miller, R.; Joos, P. *Colloid Polym. Sci.* **1994**, *272*, 731.

(27) Dukhin, S. S.; Mishchuk, N. A.; Fainerman, V. B.; Miller, R. *Colloids Surf. A* **1998**, *18*, 51.

(28) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*, 2nd ed.; Marcel Dekker: New York, 1986.

(29) Bogoslovsky, B. M. *J. Gen. Chem.* **1946**, *16*, 193; *Chem Abstr.* **1947**, *41*, 1041.

Surface tensions were measured by using the du Nouy ring, Wilhelmy plate (Kruss, K10T, Pt/Ir ring, Pt plate), and maximum bubble pressure (Sensadyne, 4.0 mm and 0.5 mm diameter tips) methods. Surface tension measurements using the du Nouy ring and Wilhelmy plate methods were performed as follows. First, 10 mL of solution was prepared by diluting stock solutions of BTHA and SDS. The solution and a small stir bar (Fisher, 14-511-68) were then transferred to the tensiometer vessel. The vessel was allowed to equilibrate at 25 °C for 5 min in the tensiometer chamber before the surface tension was measured. The vessel was then removed and illuminated with the pen lamp while stirring for 3 min. The vessel was returned to the chamber and allowed to re-equilibrate at 25 °C for 5 min before the surface tension was measured again. Successive measurements of the UV-vis absorption spectra of the solutions were used to demonstrate that the photostationary state of BTHA had been reached after the 3 min of illumination.

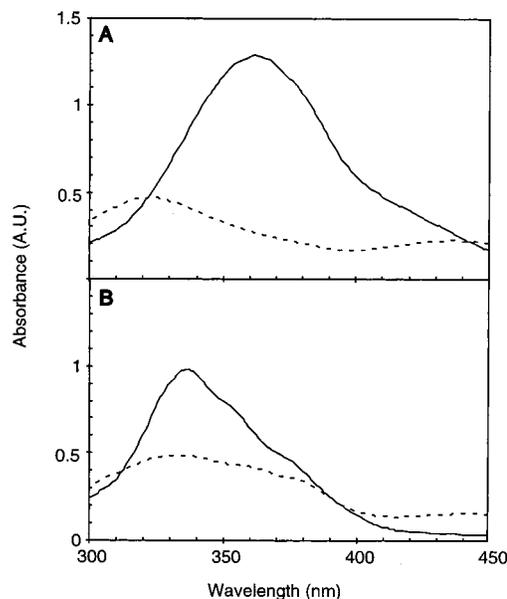
Dynamic light-scattering measurements were performed using a Brookhaven BI 9000-AT digital correlator (Brookhaven Instruments, Holtsville, NY) and a 400 mW laser (532 nm, Coherent DPSS 532-400). Both SDS and BTHA were first dissolved separately in ethanol, filtered through a 0.22  $\mu\text{m}$  filter, and recrystallized to remove dust. Aqueous solutions were prepared using water filtered through a 0.22  $\mu\text{m}$  filter. Solutions of BTHA were illuminated with light from the laser to determine if it would cause isomerization of BTHA. No isomerization occurred after  $\sim 30$  min of exposure to the laser light. We also confirmed that the surfactant in both the *cis* and *trans* states does not absorb light at 532 nm. All samples were centrifuged for 2 h and allowed to equilibrate at 25 °C for 3 min before measurements were performed. The angle of the detector was set at 90°. The autocorrelation curves were analyzed by using CONTIN.<sup>30</sup>

Pendant drop experiments were performed using a blunt 22 gauge needle attached to an electronic pipettor (Matrix, Lowell, MA). An external switch was wired to the trigger so that the drop could be dispensed without disturbing the needle. Each drop was formed by the same procedure. First, the syringe tip was filled with 12.0  $\mu\text{L}$  of the mixed surfactant solution; 9.5  $\mu\text{L}$  was dispensed to form a drop. The HgXe UV lamp was turned on to trigger the release of the drop 15, 30, or 45 s after forming the drop.

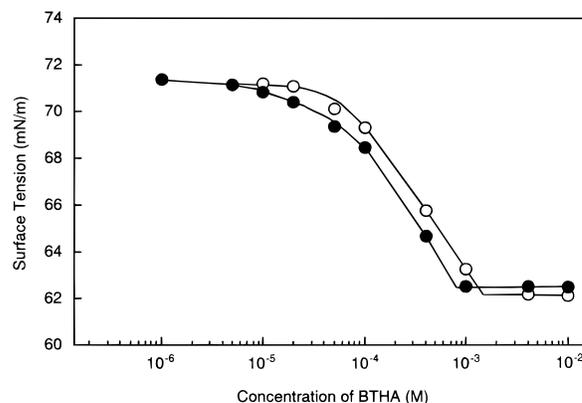
Pendant drop experiments were performed using an array of five glass capillaries (Fisher, 21-164-2G) into which were inserted wires to act as plungers. The wires were glued together in order to withdraw and dispense the same amount of liquid from each capillary. Small holes punched in cardboard were used to expose select drops to UV light from the pen lamp. The tips of the capillaries were treated with octadecyltrichlorosilane to prevent wetting of the tips by the aqueous solutions of surfactants. All pendant drop experiments were performed using a solution of 0.04 mM BTHA, 0.16 mM SDS, and 0.1 M NaCl and were recorded using a CCD camera (Sony) and a VCR (Mitsubishi).

## Results and Discussion

We first confirmed that illumination of a solution of *trans*-BTHA with UV light (pen lamp) lead to formation of *cis*-BTHA. The change in relative concentrations of the *trans* and *cis* isomers in an aqueous solution of BTHA was followed by measurement of UV-vis absorption spectra. The absorption spectra of solutions containing *trans* isomers (prior to illumination with UV light) and a mixture of *trans* and *cis* isomers (after illumination with UV light) are shown in Figure 2A. Neither solution contains aggregates (as determined by light scattering). The extent of decrease in the absorption peak at 360 nm and a comparison to other azobenzene compounds in water<sup>19</sup> lead us to estimate that  $\sim 80\%$  of the BTHA was transformed to the *cis* isomer upon illumination with UV light from the pen lamp. When SDS was added to a solution of BTHA, the absorption peak of the *trans* isomer was measured to shift to shorter wavelengths (Figure 2B). This



**Figure 2.** UV-vis absorption spectra of aqueous solutions of (A) BTHA (0.05 mM) and (B) BTHA (0.05 mM) and SDS (1.6 mM) before (solid) and after (dashed) 3 min of illumination with UV light.



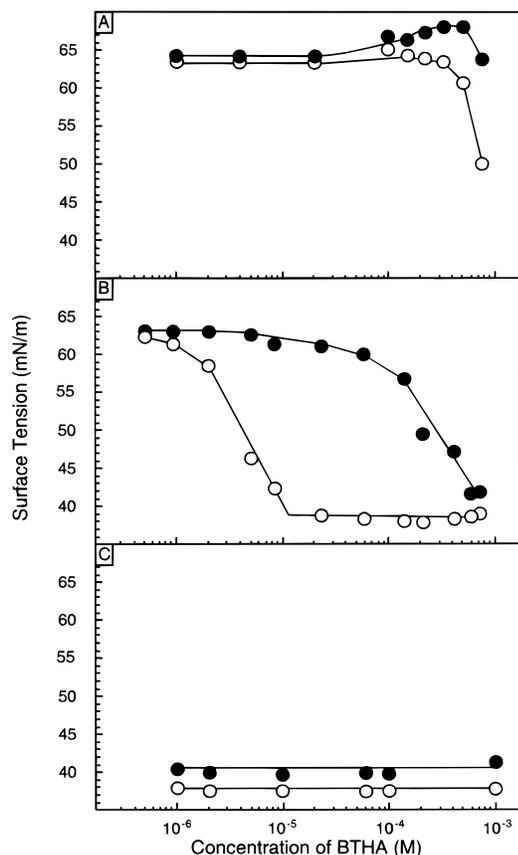
**Figure 3.** Dynamic surface tensions of aqueous solutions of BTHA measured as a function of BTHA concentration using a du Nouy ring before (filled circles) and after (open circles) illumination with UV light. The measurements were performed in the presence of 0.1 M  $\text{Li}_2\text{SO}_4$  and at 25 °C.

hypsochromic shift is due to the formation of aggregates.<sup>31</sup> A similar shift in the peak absorbance can be caused by addition of a simple electrolyte (e.g., 0.1 M NaCl) to aqueous solutions of BTHA. Addition of a cationic surfactant, such as 1 mM CTAB, does not cause a shift in the position of the absorption maxima. Illumination of pre-mixed BTHA and SDS solutions produced similar UV-vis spectra as compared with those of solutions made with SDS and preilluminated BTHA of the same concentration. These experiments show that illumination of BTHA in the presence of aggregates leads to similar extents of isomerization as compared with those of BTHA without aggregates.

Measurements of the dynamic surface tensions of aqueous solutions (0.1 M  $\text{Li}_2\text{SO}_4$ ) of BTHA using the du Nouy ring method revealed a small increase in dynamic surface tension upon illumination with UV light (Figure 3). Note that we added  $\text{Li}_2\text{SO}_4$  to these solutions so as to minimize the amount of BTHA needed for each measure-

(30) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

(31) Kuokkanen, T.; Sarpola, S. *Acta Chem. Scand.* **1994**, *48*(3), 258.



**Figure 4.** Surface tensions of aqueous solutions of mixtures of BTHA and SDS (1.6 mM) measured as a function of BTHA concentration before illumination (filled circles) and after (open circles) illumination with UV light: (A) maximum bubble pressure method; (B) du Nouy ring method; (C) Wilhelmy plate method. All measurements were performed at 25 °C.

ment. Measurements of the change in dynamic surface tension without added electrolyte were similar to those measurements with added electrolyte. The small change in dynamic surface tension measured using BTHA is similar to that reported by Hayashita for the single-headed azobenzene-based surfactant.<sup>19</sup>

When BTHA was combined with SDS in aqueous solution (no added electrolyte), however, the dynamic surface tension was found to be affected greatly by illumination with UV light. Figure 4A and B shows dynamic surface tensions of solutions of SDS and BTHA measured as a function of BTHA concentration by using the MBP and du Nouy ring methods. The concentration of SDS in solution was fixed at 1.6 mM for all measurements shown in Figure 4. Prior to illumination, the dynamic surface tensions measured using the MBP method were  $\sim 65$  mN/m over the range of concentrations of BTHA reported in Figure 4A. This high value of surface tension indicates that the amount of surfactant that adsorbed to the surface of the solution during these measurements was not sufficient to decrease the surface tension. In contrast to the case of the MBP measurements, equilibrium values of surface tensions measured by the Wilhelmy plate method (Figure 4C) were  $\sim 40$  mN/m over a similar range of BTHA concentrations. These equilibrium measurements were reached after minutes or hours and correspond to surfaces that are laden with surfactant. At the intermediate time scales measured by the du Nouy ring method (Figure 4B), dynamic surface tensions at low concentrations ( $10^{-6}$  M BTHA) were similar to those

measured with the MBP method ( $\sim 65$  mN/m) whereas, at high concentrations ( $10^{-3}$  M BTHA), the surface tensions were similar to equilibrium values measured by the Wilhelmy plate method. When combined, these measurements of surface tension indicate that the du Nouy, MBP and Wilhelmy methods characterize surfaces of these surfactant solutions with different effective "ages".

The three sets of measurements in Figure 4 also show that the measured response of the solutions to illumination varies greatly with the method used to measure surface tension. Whereas Figure 4B shows that illumination can lead to a large reduction in the magnitude of dynamic surface tensions measured by the du Nouy ring method ( $\sim 25$  mN/m at the concentration of BTHA 0.02 mM), the surface tensions measured by the MBP and Wilhelmy plate methods are affected little by illumination. This point is emphasized when comparing surface tensions of solutions with the same surfactant concentrations. For example, the surface tensions of solutions of  $10^{-4}$  M BTHA and 1.6 mM SDS before and after illumination, as measured by the MBP method, are 67 and 65 mN/m, respectively. The surface tensions of the same solutions measured using the Wilhelmy plate method before and after illumination are 41 and 38 mN/m, respectively. In contrast, the du Nouy ring method reports the surface tension before and after illumination to be 58 and 38 mN/m, respectively. We interpret these measurements to indicate that when using the MBP method, the amount of surfactant adsorbed at the surface of each bubble is small both before and after illumination and thus the surface tensions measured are high ( $\sim 65$ – $70$  mN/m). In contrast, the equilibrium states (Wilhelmy plate method) of these surfaces are ones that are laden with surfactant and thus possess low surface tensions ( $\sim 40$  mN/m). It is only for the case of dynamic surface tensions measured by the du Nouy ring that we observe illuminated solutions to have much lower surface tensions than solutions that have not been illuminated.

We hypothesized that the low dynamic surface tensions of the illuminated solutions can be understood in terms of a change in the aggregation state of the surfactant. A change in the number density of aggregates, or size of aggregates, or both, would lead to a change in the rate of mass transport of surfactant to the interface (eq 1). We investigated the effect of illumination on the state of aggregation of BTHA and SDS in bulk solution by using light-scattering measurements. Dynamic light-scattering measurements were performed using solutions of 0.1 mM *trans*-BTHA and 1.6 mM SDS. Solutions were centrifuged for 2 h and then placed in a thermostated bath for 5 min before measurements were taken. The hydrodynamic diameters of aggregates were measured to be  $150 \pm 10$  nm, and the scattered intensity of light was 2500 kcnts/s. The samples were then illuminated with UV light for 3 min and returned to the bath for 5 min. The aggregates in the illuminated sample were similar in size ( $140 \pm 10$  nm diameter) to the nonilluminated sample. However, the scattering intensity was lower by almost a factor of 2 (1480 kcnts/s). Because the intensity of light scattered from aggregates in solution is proportional to their number density,<sup>32</sup> the solution after illumination has roughly half the number density of aggregates as compared to the solution prior to illumination. These measurements support our hypothesis that light-induced changes in the extent of aggregation of surfactants contribute to the influence of light on the dynamic surface tensions of these solutions.

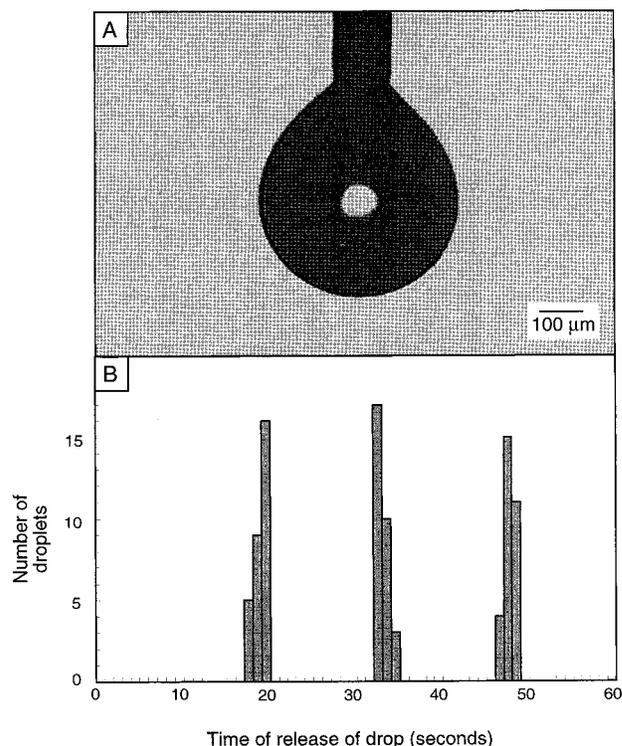
(32) Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1985; Chapter 2.

The proposed connection between the state of aggregation of surfactant in solution and the dynamic surface tension is also supported by the rise in dynamic surface tension that accompanies the addition of BTHA to a solution of SDS, as shown in Figure 4A. At low concentrations of BTHA, the dynamic surface tension is dominated by the concentration of monomeric SDS. The addition of BTHA causes the formation of aggregates of BTHA and SDS, thereby reducing the concentration of monomeric SDS. The lowering of the concentration of monomeric SDS decreases the rate of transport of SDS to the interface and leads to an increase in dynamic surface tension. This effect is greatest at a concentration of BTHA ( $\sim 0.8$  mM) which is half the concentration of SDS (1.6 mM). The 2:1 ratio of concentrations plausibly corresponds to the formation of electrically neutral aggregates and a minimum in monomer concentration.

For aggregates as large as those reported here, a change in the number density of aggregates by a factor of 2 will lead to a large change in the monomer (or small aggregate) concentration. Using values of  $c = 0.3$  mM,  $\Gamma^{-1} = 50$  Å<sup>2</sup> molecule<sup>-1</sup>, and  $D = 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, eq 1 predicts a characteristic diffusion time of  $\sim 100$  s. That is, when transport of surfactant to the interface is controlled by the diffusion of aggregates, it takes approximately  $\sim 100$  s to transport a sufficient number of surfactant molecules to the surface to form a monolayer and thereby lower the surface tension. Following illumination, under conditions where transport is plausibly dominated by diffusion of monomeric surfactant to the interface ( $D \sim 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>), the characteristic diffusion time decreases to  $\sim 1$  s. While these estimates of characteristic diffusion times depend on our choice of  $c$  and  $\Gamma$ , the principal point of this discussion is to highlight the fact that changes in the aggregation of surfactant in solution can change the time required to transport surfactant to the surfaces of solutions by almost two decades.

The experimental results above demonstrate that light can be used to control dynamic surface tensions of solutions of BTHA and SDS on time scales of seconds. Here we illustrate the utility of light-induced changes in surface tensions by triggering the release of pendant droplets of solutions by illumination with light (Figure 5). Without illumination, the rate of decrease of the surface tension is low, causing the drops release after 60 s or more. However, illumination of the droplets at the times 15, 30, or 45 s after their formation lead to their release within a few seconds of the onset of illumination. The shape of the droplet was observed to change within  $\sim 1$  s of the onset of illumination. After 3–5 s, the surface tension was sufficiently low to allow release of the pendant drop. These results demonstrate that the characteristic time over which the surface tension of the solution relaxes can be decreased by more than an order of magnitude upon illumination.

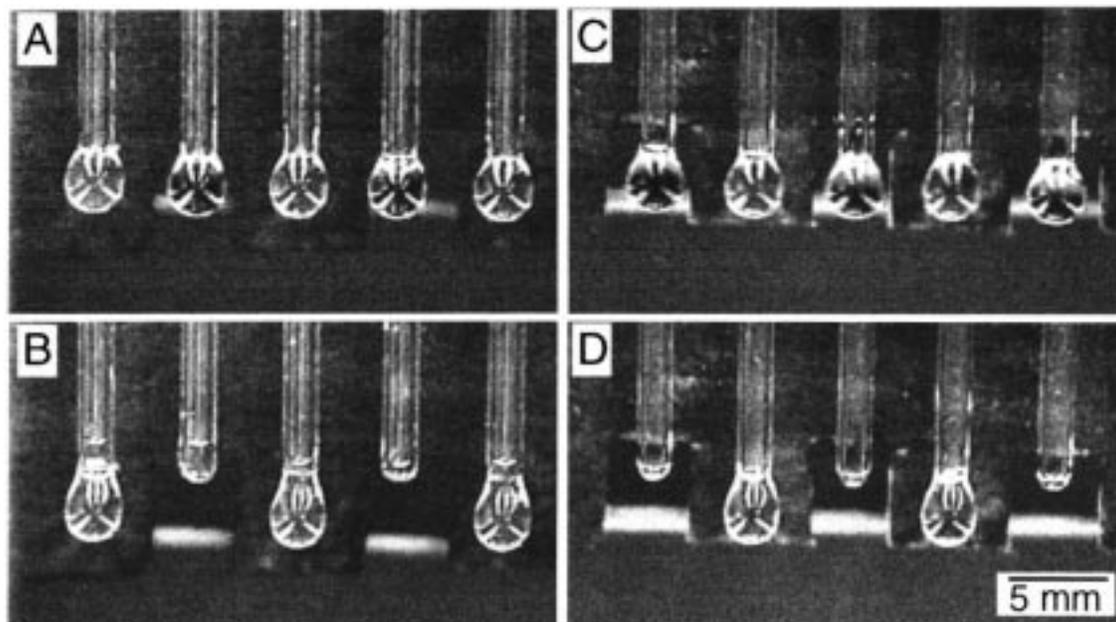
We also demonstrate the usefulness of light-induced lowering of surface tension by using UV light to address a simple array of capillaries and thereby select the release of droplets from particular capillaries within the array. Figure 6A and C shows five pendant droplets formed at the ends of five capillaries. When light is patterned on this array, particular droplets can be released upon demand. Illumination of the second and fourth droplets (Figure 6A) caused their release from the capillary (Figure 6B) while the first, third, and fifth drops remained attached for at least another 25 s. Alternatively, illumination of the first, third, and fifth drops (Figure 6C) selectively



**Figure 5.** Timed release of a pendant droplet of aqueous solution (0.04 mM BTHA, 0.16 mM SDS, and 0.1 M NaCl) from a capillary by using UV light: (A) image of pendant drop (9.50 μL) suspended from the end of a capillary; (B) distribution of lifetimes of droplets following their illumination at 15, 30, and 45 s.

released these drops (Figure 6D) from the array of capillaries. We observed the rate of release of the pendant droplets to be a function of the intensity of the incident UV light: the release for the pen lamp was slower than that for the Xe lamp. These results suggest that small drops and focused light sources will permit droplets to be released at rates that are substantially faster than those reported in this paper. Control experiments performed with single drops and arrays of capillaries demonstrate that light-induced triggering of the release of drops does not occur for drops formed from pure water or for surfactant solutions containing only SDS.

The light-sensitive surfactant system described in this paper demonstrates a new principle for active control of dynamic surface tensions of aqueous solutions. The principle reported here is based on the use of light to control the state of aggregation of surfactant within solution and thus its rate of delivery onto a surface. This principle contrasts those reported in two past studies based on redox-active surfactants (see Introduction). For example, past studies of the influence of the oxidation state of ferrocenyl surfactant on the surface properties of aqueous solutions can be largely described in terms of the equality of the chemical potential of the surfactant in the bulk and at the interface (i.e., equilibrium partitioning between the surface and bulk).<sup>4–9</sup> In contrast, the effects of transforming disulfide surfactants into thiol fragments can be traced to the formation of a reaction-induced nonequilibrium surface excess of thiol fragments.<sup>10</sup> The results of these past investigations, when combined with the light-sensitive surfactant described herein, provide three general principles of active control of surfactant solutions.



**Figure 6.** Light-directed release of droplets of aqueous solutions containing 0.04 mM BTHA, 0.16 mM SDS, and 0.1 M NaCl from an array of five capillaries: (A) image of five pendant drops poised at the end of capillaries; (B) image of capillaries in part A after illumination of two drops with UV light; (C) image of five pendant drops using the same capillaries; (D) image of capillaries in part C after illumination of three drops with UV light.

### Conclusion

The principal result of this paper is a demonstration of the use of light to control the dynamic surface tension of a mixed surfactant system formed from SDS and the light-sensitive, cationic surfactant BTHA. By comparing the dynamic surface tensions of aqueous solutions of these surfactants before and after illumination with UV light, we demonstrate that illumination causes the surface tensions of these solutions to decrease at rates that are 1–2 orders of magnitude faster than the rate of reduction of surface tension without prior illumination. For example, by using the du Nouy ring method, the dynamic surface tension of a solution of  $10^{-4}$  M BTHA and 1.6 mM SDS measured before and after illumination was found to differ by as much as 25 mN/m. Dynamic light-scattering measurements support our hypothesis that a light-induced

decrease in the extent of aggregation of surfactant leads to a change in the characteristic time required to transport surfactant to the surface of the solution. The usefulness of light-induced changes in dynamic surface tension is demonstrated by spatial and temporal control of the release of droplets of aqueous solution from arrays of capillaries.

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