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# Photoresponsive Foams Generated by a Rigid Surfactant Derived from

# **Dehydroabietic Acid**

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# ABSTRACT

Innovation in the structure of surfactants is crucial to the construction of a surfactant-based system with intriguing properties. With dehydroabietic acid as a starting material, a nearly totally rigid azobenzene surfactant (R-azo-Na) was synthesized. The *trans*-R-azo-Na formed stable foams with half-lives of 636, 656, 976, and 872 min for 0.3, 1, 2, and 4 mmol·L<sup>-1</sup> aqueous solutions, respectively. Under UV light irradiation, a fast collapse of the foams was observed, showing an in situ response. The excellent foam stability of *trans*-R-azo-Na leads to the extremely high photoresponsive efficiency. As revealed by dynamic surface tension and pulsed-field gradient NMR methods, an obvious energy barrier existed in the adsorption/desorption process of *trans*-R-azo-Na on the air/water interface. The foams formed by *trans*-R-azo-Na are thus stable against coarsening processes. The results reveal the unique photoresponsive behavior of a surfactant with a rigid hydrophobic skeleton and provide new insights into the structure causing aggregation of surfactants.

KEYWORDS: Dehydroabietic acid, Photoresponsive foams, rigid surfactant, azobenzene

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# Introduction

Surfactants that are responsive to external stimuli, such as  $pH^{1-4}$ , electrolyte<sup>5-6</sup>, magnetic field<sup>7</sup>, temperature<sup>8-9</sup>, light<sup>3, 10-11</sup>, and  $CO_2/N_2^{12-14}$ , have received substantial attention in recent years<sup>15</sup>. Numerous smart systems, such as emulsions<sup>16-17</sup>, viscoelastic solutions<sup>18-22</sup> and foams<sup>23-27</sup>, have been developed using these surfactants and have shown attractive stimuli-responsive behaviors. Among all the triggers investigated, light irradiation is particularly attractive. First, it does not pollute the surfactant solutions<sup>28</sup> and can be operated in a clean environment<sup>29</sup>. Second, light irradiation can be directed at a precise spatial location. These features are especially suitable to control foams, which are heterogeneous and occupy massive space. Aqueous foams are metastable systems with dispersed gases separately wrapped by thin liquid films, where surfactants are often used as foaming agents and foam stabilizers<sup>30-31</sup>. Investigations on foamability and foam stabilities are important in both theory and applications. While in some industrial processes, such as foam flooding and foam flotation, defoaming is also a crucial step for smooth processing. The addition of antifoaming agents is one of the traditional methods to eliminate previously produced foams. However, it does not only bring out changes to the system composition but also hinders the regeneration of foams, which is unfavorable in some cyclic processes. The foam systems that respond to external stimuli<sup>32-37</sup>, such as light, can overcome the above shortcomings and have shown promising behaviors in potential applications as recently reported<sup>38-42</sup>.

In a photoresponsive foam system, the efficiency of response, that is, the discrepancy in the foam stability caused by light, is the key characteristic that is concerned. Significant discrepancy in foam stability before and after light irradiation indicates high photoresponsive efficiency. The development of highly effective photoresponsive foam systems is beneficial for practical applications. Azobenzene is a popular group with good reversibility that is widely used in photoresponsive systems<sup>43-45</sup>. It has a rigid skeleton, which can experience *trans-cis* isomerization under UV/Vis light irradiation. The photoresponsive properties of a system containing an azobenzene surfactant mainly rely on the configuration change caused by the azobenzene isomerization. Inspecting the available investigated foam systems, it can be seen that the azobenzene surfactants utilized all contain flexible alkyl chains. To lower the free energy of the

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system, the alkyl chains may twist or bend in solution, which weakens the light-triggered changes in the molecular configuration to some extent. In contrast, if the hydrophobic skeleton of an azobenzene surfactant is totally rigid, it can fully express the effect of the molecular configuration change and is expected to achieve a remarkable photoresponsive efficiency. To the best of our knowledge, studies about photoresponsive surfactants with totally rigid hydrophobic skeletons for use in foam systems have never been reported.

The synthesis of a rigid surfactant with satisfactory surface activity remains challenging. Fortunately, nature gives us the opportunity to examine our thoughts. Rosin, a secretion of pine, is composed mainly of abietic acids with rigid tricyclic structures. Dehydroabietic acid is one of the important derivatives of rosin with favorable chemical stability. With this rigid acid as a starting material, a nearly totally rigid surfactant containing an azobenzene group (R-azo-Na, shown in Scheme 1) was synthesized. The photoresponsive properties of foams generated by R-azo-Na were investigated. Since R-azo-Na is a water-soluble surfactant with a rigid structure, the results obtained are beneficial to understand the peculiar self-assembly principles of rigid surfactants.



Scheme 1. The synthetic scheme of R-azo-Na.

# **Experimental section**

Materials

Disproportionated rosin (containing 42.5% dehydroabietic acid, technical grade) was purchased from Nanjing Pine Forests Chemistry Co., Ltd. Ethyl 2-bromoacetate (>98%) was obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All other solvents and reagents were of analytical grade and used without further purification.

#### Synthesis

The reaction scheme is shown in Scheme 1. The detailed synthetic processes are included in the Supporting Information. The brief synthetic procedure is described as follows.

Dehydroabietic acid was first purified to reach a purity of 97.9% in our lab. Methyl dehydroabietate (1) was synthesized by the reaction of dehydroabietic acid and SOCl<sub>2</sub> and anhydrous methanol at 60 °C. Methyl dehydroabietate reacted with NBS at room temperature for 7 hours to obtain methyl 12-bromo-dehydroabietate (2), which was then mixed with nitric acid (88%) sulfuric (95-97%)and concentrated acid to obtain 12-bromo-13-nitro-deisopropyldehydroabietate (3). Methyl 13-aminodeisopropyldehydroabietate (4) was obtained by the reduction of 12-bromo-13-nitro-deisopropyldehydroabietate with  $H_2$  with a Pd/C catalyst. An aqueous solution of sodium nitrite was dropped onto a mixture of concentrated hydrochloric acid and methyl 13-aminodeisopropyldehydroabietate below 5 °C to obtain a diazonium salt, which was then added to the aqueous solution of sodium phenolate to obtain R-azo-OH. R-azo-Et was obtained by the reaction of R-azo-OH and ethyl 2-bromoacetate at 60 °C in DMF. The target material R-azo-Na was obtained as an orange solid after saponification of R-azo-Et with NaOH and then dried under vacuum. The <sup>1</sup>H NMR was then used to reveal the chemical shifts of the protons attaching with the carbon atoms in the R-azo-Na molecules. The number of carbon atoms has been denoted in Scheme 1. The number in front of H indicates the number of H atoms at the position. <sup>1</sup>H NMR (400 MHz, MeOD)  $\delta$  7.84 (d, 2H, C20-1H, C24-1H), 7.61 (d, 1H, C12-1H), 7.53 (s, 1H, C14-1H), 7.41 (d, 1H, C11-1H), 7.06 (d, 2H, C21, 23-2H), 4.47 (s, 2H, C25-2H), 3.67 (s, 3H, C16-3H), 3.04-2.88 (m, 2H, C7-2H), 2.42 (d, 1H, C1-1H), 2.21 (dt, 1H, C5-1H), 1.95 – 1.66 (m, 5H, C2-2H, C3-2H, C6-1H), 1.46 (dt, 2H, C1-1H, C6-1H), 1.29 (d, 6H, C17,18-6H); HRMS Calcd for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O<sub>5</sub>Na [M-Na]<sup>-</sup>: 449.2082; Found: 449.2083. Light irradiation

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The light irradiation experiments were carried out with an IWATA UV-201SA point light (9 W) (Japan) for a set period of time.

#### **UV-Vis spectra**

The UV-Vis spectra of the aqueous solutions of R-azo-Na before and after UV light irradiation were obtained with a double-beam UV-visible light spectrophotometer TU-1901 (Beijing Purkinje General Instrument Co., Ltd.) between 250 and 550 nm. For monitoring the photoisomerization purpose, the sample was first diluted to be measured.

#### NMR measurements

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were carried out with a Bruker Advance III 400 MHz spectrometer (Bruker, Switzerland) on samples in 0.5 mL MeOD at 25 °C. In addition, the <sup>1</sup>HNMR of R-azo-Na at the photostationary state after UV light irradiation was recorded by dissolving the R-azo-Na in 0.5 mL MeOD and irradiating with UV light for 10 min. The self-diffusion coefficient of R-azo-Na at 0.1 mmol·L<sup>-1</sup> was measured with a Bruker 600 MHz spectrometer (Bruker, Switzerland) on samples in D<sub>2</sub>O (pH = 12) at 25 °C.

#### Equilibrium and dynamic surface tensions

All prepared surfactant solutions were adjusted to pH = 12 with NaOH to prevent the hydrolysis of R-azo-Na. The equilibrium surface tensions before and after UV light irradiation were measured using the du Noüy ring method<sup>46</sup> at 25 °C. The photostationary state of the R-azo-Na solutions after UV light irradiation was assured by measuring their UV-Vis spectra. The dynamic surface tensions of R-azo-Na isomers were measured with a SITA science line t100 tensiometer (Germany) at different temperatures.

#### **Fluorescence measurements**

Nile red was selected as a fluorescence probe. Fluorescence measurements of different concentrations of R-azo-Na (pH = 12) before and after UV light irradiation were carried out with a Cary Eclipse fluorospectrophotometer (USA). The excitation wavelength and emission wavelength used were 540 nm and 550 nm, respectively. The bandwidths of both slits were set to 5 nm.

#### Foam investigation and light irradiation

Aqueous solutions (5 mL) of R-azo-Na and SDS at different concentrations were prepared in 50 mL volumetric cylinders with plugs. The volumetric cylinders were shaken up and down 25 times to generate the foams. The changes of volumes including water volume fraction of the foams formed by *trans*-R-azo-Na and SDS with time were recorded. To investigate the foam size, the sample of the foam was placed on a microscope slide and was observed using a VHX-1000 microscope system (Keyence Co.). The surface dilational measurements on *trans*-R-azo-Na and SDS were carried out using an optical angle meter OCA-20 with oscillating drop accessory ODG-20 (DataPhysics). For light irradiation purposes, 5 mL of aqueous surfactant solutions of *trans*-R-azo-Na at different concentrations were prepared in 26.5-mL quartz tubes (15 cm (h) × 1.5 cm (d)). The quartz tubes were shaken up and down 25 times to generate the foams, which were then irradiated with a UV light beam perpendicular to the tube at a distance of about 1.5 cm.

#### **Results and discussion**

Photoresponsive properties of R-azo-Na in aqueous solutions



**Figure 1.** UV-Vis spectrum of R-azo-Na solutions of 4 mmol·L<sup>-1</sup> under UV/Vis light irradiation.

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**Figure 2.** <sup>1</sup>H NMR spectra (in  $CD_3OD$ ) for (a) *trans*-R-azo-Na; (b) R-azo-Na at the photostationary state after UV light irradiation. The seven protons of the azobenzene group are assigned by the letters a-g.

It is known that one shortcoming of the conventional carboxylate surfactants with large hydrophobic groups is their poor solubility in water<sup>47</sup>. R-azo-Na is a carboxylate surfactant containing 26 carbon atoms with one head group. We initially assumed that the solubility of R-azo-Na would be bad. To our surprise, R-azo-Na solubilized well in water at room temperature. The solubility measured at 25 °C was 88 mmol·L<sup>-1</sup> using a standard curve method (Supporting Information Figure S13). The rather good water solubility of R-azo-Na may arise from its nonplanar rigid structure, which is hard to stack in order. The tendency of precipitation is thus depressed.

As a surfactant that contains an azobenzene group, R-azo-Na could change its configuration in response to light irradiation of certain wavelength. The photoisomerization of R-azo-Na can be monitored with UV-Vis spectroscopy. As shown in Figure 1, the maximum of the characteristic adsorption band of *trans*-R-azo-Na appears at 352 nm. After UV light irradiation for 20 s, the peak at 352 nm was depressed. When the sample was irradiated with the UV light for 2 min, the peak at 352 nm was greatly depressed and a peak at 440 nm arose, indicating the transformation of most *trans*-R-azo-Na to its *cis* form. Further irradiation for 5 min caused almost no change. It can be

concluded that for 4 mmol·L<sup>-1</sup> solution of R-azo-Na, the photostationary state was achieved by irradiating with UV light for 2 min. Furthermore, the original solution state rich in trans-R-azo-Na molecules can mostly be restored by the sequential visible light irradiation for 10 min. To estimate the ratio of *cis*-R-azo-Na to *trans*-R-azo-Na at the photostationary state. <sup>1</sup>H NMR measurements were carried out on the same sample dissolved in CD<sub>3</sub>OD before and after UV light irradiation. As shown in Figure 2(a), the proton signals of the phenyl rings contained in *trans*-R-azo-Na are present downfield. This is caused by the delocalization of the  $\pi$  electrons across the planar trans-azobenzene group, enhancing the deshielding effect of the phenyl rings. When the azobenzene group was transformed to its *cis* form under UV light irradiation, the conjugated planar structure of the azobenzene was destroyed. The  $\pi$  electrons of *cis*-azobenzene merely delocalize at their separate phenyl rings, leading to an upfield shift of the proton signals. Comparing the <sup>1</sup>H NMR spectra of R-azo-Na before and after UV light irradiation, it is clear that most trans-R-azo-Na were transformed to cis-R-azo-Na. In Figure 2(b), it is also found that the chemical shifts of one specific proton locate at different positions, which correspond to the presence of cis-R-azo-Na and the remaining trans-R-azo-Na, respectively. According to the integration, the cis isomer of R-azo-Na is estimated to be at 95.2% of the photostationary state.



**Figure 3.** Apparent surface tensions of aqueous R-azo-Na solutions (pH = 12) as a function of the surfactant concentration at 25 °C( $\blacksquare$ , before UV light irradiation;  $\Box$ , after UV light irradiation).

Table 1. The surface-active parameters of aqueous solutions of R-azo-Na at 25 °C. (a: du No	üy
ring method; b: fluorescence probe method)	

	$cmc/(mmol \cdot L^{-1})$	$C_{20}/(\text{mmol}\cdot\text{L}^{-1})$	$\gamma_{\rm cmc}/({\rm mN}\cdot{\rm m}^{-1})$
Before UV light irradiation	0.27 <sup>a</sup> , 0.28 <sup>b</sup>	0.14	44.3
After UV light irradiation	1.59 <sup>a</sup> , 1.72 <sup>b</sup>	1.19	44.8

The apparent equilibrium surface tensions of R-azo-Na before and after UV light irradiation are shown in Figure 3. The cmc values were further confirmed by the fluorescence probe method with Nile red (Supporting Information Figure S14). The surface-active parameters are listed in Table 1. The critical micelle concentration of *trans*-R-azo-Na was 0.27 mmol·L<sup>-1</sup>. After the UV light irradiation, most R-azo-Na was transformed to its cis form, and the critical micelle concentration increased to  $1.59 \text{ mmol}\cdot\text{L}^{-1}$ . The UV light irradiation caused an approximately 6-fold change in the cmc of R-azo-Na, revealing a significant aggregation discrepancy before and after UV light irradiation. Hayashita et al. investigated a series of cationic azobenzene surfactants<sup>48</sup> with different alkyl chain lengths and spacers. The largest ratio of cmccis and cmctrans was found to be 4.1. This comparison verifies the advantage of a rigid surfactant in the photoresponsive behavior. In an azobenzene surfactant with a totally rigid skeleton, the relative positions of the atoms are fixed. Even the furthest group from azobenzene can be affected by the isomerization. In contrast, the flexible alkyl chains contained in an azobenzene surfactant may adjust their relative positions to the azobenzene group by twist or bending according to the surroundings when isomerization occurs. The photoresponsive efficiency is thus lowered. Of course, the rigidity of a surfactant is not advantageous in every aspect. Due to the bulkiness of the rigid skeleton, R-azo-Na showed a weak ability in lowering the surface tension. The  $\gamma_{\rm cmc}$  (surface tension at the critical micelle concentration) before and after UV light irradiation was 44.3 mN·m<sup>-1</sup> and 44.8 mN·m<sup>-1</sup>, respectively, which is significantly higher than those of conventional surfactants<sup>49</sup>.

Photoresponsive properties of foams generated by R-azo-Na



**Figure 4.** Digital photographs of aqueous foams formed by different concentrations of *trans*-R-azo-Na solutions and 4 mmol·L<sup>-1</sup> SDS solution. Surfactant concentrations of *trans*-R-azo-Na from a to d are 0.3, 1, 2, and 4 mmol·L<sup>-1</sup>, respectively.

To evaluate the photoresponsive efficiency of R-azo-Na, the foams generated by *trans*-R-azo-Na was first investigated. The behavior of the commercially available surfactant SDS was also investigated for comparison. As shown in Figure 4, after vigorous shaking by hand, *trans*-R-azo-Na of several concentrations (above the *cmc*) all formed foams with small gas bubbles trapped in aqueous solutions. The original volumes of the foams were 8, 12, 14, and 17 mL for 0.3, 1, 2, and 4 mmol·L<sup>-1</sup>, respectively, increasing with surfactant concentrations. Comparatively, the formability of SDS was rather strong, as shown by a foam volume of 39 mL at 4 mmol·L<sup>-1</sup> and 47 mL at 20 mmol·L<sup>-1</sup> (Supporting Information Figure S15). This is attributed to the rather low  $\gamma_{cmc}$  of SDS, which is in favor of the surfactant formability.

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**Figure 5.** Volume variation of foams stabilized by *trans*-R-azo-Na at different concentrations over time at 25 °C( $\Box$ , 0.3 mmol·L<sup>-1</sup>;  $\triangle$ , 1 mmol·L<sup>-1</sup>;  $\bigcirc$ , 2 mmol·L<sup>-1</sup>;  $\bigtriangledown$ , 4 mmol·L<sup>-1</sup>).

The half-life  $t_{1/2}$ , which indicates the time required for the collapse of the foam to half of its initial height or volume<sup>50</sup>, was used to estimate the foam stability. As shown in Figure 5, the half-life  $t_{1/2}$  was 636, 656, 976, and 872 min for 0.3, 1, 2, and 4 mmol·L<sup>-1</sup> trans-R-azo-Na aqueous solutions, respectively. To the best of our knowledge, trans-R-azo-Na forms the most stable foams among the azobenzene-containing surfactants up to now. On the other hand, the half-life  $t_{1/2}$  of the aqueous foams stabilized by SDS at 4 mmol·L<sup>-1</sup> and 20 mmol·L<sup>-1</sup> was 283 and 257 min, respectively (Supporting Information Figure S15). These results indicate that, even compared with that of the commercially available anionic surfactant, the foam stability of trans-R-azo-Na is remarkable<sup>30</sup>. It is believed that the surface dilational elasticity is relevant with the foam stability. The reason was first revealed by the comparative measurements of the surface dilational elasticity of both surfactants, which was expected to reveal the difference in molecular interactions at the interface. It is reported that the surface dilational elasticity of SDS is usually higher than the actual value because of the presence of impurities<sup>51-52</sup>. However, even in this way, the surface dilational elasticity of trans-R-azo-Na is always above that of SDS during the same frequency range at the same concentration as shown in Figure S17. This indicates that the adsorption films formed by trans-R-azo-Na is more elastic, which is critical for stabilization of foams. From Figure 4, it is also obvious that the size of the bubbles stabilized by trans-R-azo-Na is smaller than that stabilized by SDS. This phenomenon was further inspected with the microscope. As shown in

Figure 6, the average size of the bubbles stabilized by *trans*-R-azo-Na is smaller than that stabilized by SDS. The same phenomenon was even observed for the foams existing for 6 hours. Because the *trans*-R-azo-Na molecules can form foams with smaller bubble size, the foams produced thus have the stronger ability to resist the coarsening process<sup>53</sup>, which may serve as one of the factors stabilizing foams.



**Figure 6.** Micrographs of the bubbles formed by 2 mmol·L<sup>-1</sup> *trans*-R-azo-Na (a and c)solutions and 4 mmol·L<sup>-1</sup> SDS solutions (b and d). (a) and (b) were taken immediately after shaking. (c) and (d) were taken after 6 hours.



**Figure 7.** Variation of the water volume fraction in aqueous foams stabilized by *trans*-R-azo-Na and SDS solutions at different concentrations with time at 25 °C (*trans*-R-azo-Na: 0.3 mmol·L<sup>-1</sup>( $\Box$ ), 1 mmol·L<sup>-1</sup>( $\odot$ ), 2 mmol·L<sup>-1</sup> ( $\Delta$ ), 4 mmol·L<sup>-1</sup> ( $\nabla$ ); SDS: 4 mmol·L<sup>-1</sup> ( $\diamond$ ), 20 mmol·L<sup>-1</sup> ( $\bigstar$ ))

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The drainage in foams is another factor affecting the foam stability. As shown in Figure 7, for the investigated *trans*-R-azo-Na and SDS solutions of different concentrations, the volume fraction of water in foams decreased quickly in the initial 2-3 minutes and then gradually leveled off with time. The *trans*-R-azo-Na systems were able to hold a water volume fraction of around 0.025 after 200 minutes.

The photoresponsive properties of the R-azo-Na foams were then investigated in a 2 mmol·L<sup>-1</sup> solution. When the stable foams were irradiated with UV light, rapid rupture of the foams was observed, showing in situ responses to light (shown in the movie S1 in the Supporting Information). The amount of light transmitted inside foams depends on the water volume fraction in the foams<sup>39, 54-55</sup>. Since the water fraction at the foam top is smaller than that at the foam bottom, the collapse speed of foams gradually decreases. All the foams collapsed in 4 min (Supporting Information Figure S18). A similar phenomenon was reported by Monteux et  $al^{23}$ , in which the photofoams were formed with an azobenzene surfactant containing alkyl tails. However, since trans-R-azo-Na forms the most stable foams among the reported azobenzene surfactants up to now, the highest photoresponsive efficiency of the R-azo-Na foams is guaranteed. It is reported that foams responsive to heat can also respond to the stimuli of UV light because of the presence of materials that can adsorb light energy to increase the temperature<sup>39</sup>. Different with theirs, the photoresponsive behavior of foams investigated here is attributed to the *trans-cis* isomerization of the azobenzene group contained in the R-azo-Na molecule because there is no such heat-adsorbing materials in our systems. This reason was further identified by the fact that the foams formed by SDS (without an azobenzene group) are not responsive to the same UV light (shown in the movie S2 in the Supporting Information).

The work carried out by Monteux et al<sup>56</sup> indicated that when a *trans* azobenzene surfactant was transformed to the *cis* isomer, it desorbed quickly from the interface. This observation is suitable to explain the in situ response of *trans*-R-azo-Na foams to UV light. Initially, *trans*-R-azo-Na adsorbs at the air/water interface to stabilize the thin liquid films that separate the gas bubbles. Under UV light irradiation, most of the *trans*-R-azo-Na at the interface are transformed to its *cis* isomer. It is known that the *cis* isomer of R-azo-Na is more polar than the *trans* one. The resulted

*cis*-R-azo-Na desorb from the interface at the short timescale, leading to unstable films. The rapid collapse of the R-azo-Na foams was thus observed.

The foam properties of the solutions at the photostationary state after UV light irradiation, or can be called *cis*-rich R-azo-Na solutions were further investigated for understanding more details. To perform this experiment, the trans-R-azo-Na solutions were first irradiated with the UV light for at least 5 min to reach the photostationary state. It's worth noting that some trans-R-azo-Na molecules are still present in the solutions after UV light irradiation as revealed by the above <sup>1</sup>H NMR results. As shown in Figure S19, the cis-rich R-azo-Na solutions all generated foams after hand shaking, with an initial foam volume being 7, 12, 21, and 31 mL, and a half-life  $t_{1/2}$  of 18, 108, 653, and 505 min for concentration of 0.3, 1, 2, and 4 mmol·L<sup>-1</sup>, respectively. Apparently it seems that the foam properties of cis-rich R-azo-Na solutions are comparable with that of trans-R-azo-Na. However, since the trans-R-azo-Na molecules have stronger ability to adsorb at the interfaces, the foams of *cis*-rich R-azo-Na solutions are likely to be stabilized by the remaining *trans*-isomers. To prove this, the foam of 2 mmol·L<sup>-1</sup> *cis*-rich R-azo-Na solution was then irradiated with the UV light. As expected, the rapid collapse of foams indicating an in situ response was observed (shown in the movie S3 in the Supporting Information). Because the sole cis-R-azo-Na is not responsive to the UV light irradiation, this observation verifies that it's actually the remaining trans-R-azo-Na molecules that stabilize the foams of cis-rich R-azo-Na solutions. Combining the results of Monteux et al<sup>23, 56</sup>, it can be concluded that the interfacial properties of an azobenzene surfactant system are always dominated by the trans-isomers of azobenzene surfactants.

As revealed by the above results, the high photoresponsive efficiency of the R-azo-Na foams is attributed to the high foam stability of *trans*-R-azo-Na. Understanding the mechanism that stabilizes the foams in *trans*-R-azo-Na solutions is helpful to understand the responsive behaviors of totally rigid surfactants. As we know, the stability of foams is related with the stability of the thin liquid films where the surfactants adsorb. In a single-component surfactant foam system, the surfactant structure directly affects the coarsening of bubble, the drainage of the liquid in the thin films, the diffusion of gas through the thin films, the surface viscosity and the presence of an electric double layer<sup>49</sup>. Thus, the surfactant structure is extremely important in foam stability.

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R-azo-Na has a rigid molecular skeleton, which may account for the stability of the foams. The dynamic surface tensions of both *trans*-R-azo-Na solutions and *cis*-rich R-azo-Na solutions were thus investigated to determine more details.

The dynamic adsorption of surfactants from the bulk solution to a freshly formed surface is usually classified by two processes. First, the surfactant diffuses from the bulk to the subsurface. Then, a sequential adsorption from the subsurface to the surface occurs<sup>57</sup>. Compared with the diffusion process, if the timescale of adsorption from the subsurface to the surface is very fast, the adsorption kinetics are characterized as diffusion controlled. If the transfer of surfactants from the subsurface to the surface is characterized as mixed diffusion-kinetic controlled, in which an energy barrier exists. Based on the Ward-Tordai equation<sup>58</sup>, a renormalized equation that describes the diffusion process of surfactants with a potential energy barrier, is described as follows<sup>59</sup>:

$$\Gamma(t) = 2c_0 \sqrt{\frac{D_{\text{eff}}t}{\pi}} - 2\sqrt{\frac{D_{\text{eff}}}{\pi}} \int_0^{\sqrt{t}} c_s(t-\tau) \,\mathrm{d}\tau^{1/2}$$
(1)

where  $\Gamma$  is the adsorption,  $c_0$  is the bulk concentration of the solution,  $D_{\text{eff}}$  is the effective diffusion coefficient, t is the time,  $c_s$  is the subsurface concentration, and  $\tau$  is the dummy variable. In equation (1), the first term indicates that the solute transfers to the subsurface from the bulk surface, and the second term represents the solute coming back to the bulk solution as the subsurface concentration increases.

In the beginning of the adsorption,  $c_s$  is very small, and there is no back diffusion. Thus, equation (1) is simplified to the following:

$$\Gamma(t) = 2c_0 \sqrt{\frac{D_{\rm eff}t}{\pi}}$$
<sup>(2)</sup>

Combining the Gibbs adsorption equation and considering the presence of  $NaOH^{49}$ , the dynamic surface tension of R-azo-Na can be expressed as equation (3).

$$\gamma(t)_{t \to 0} = \gamma_0 - 2(1 + \frac{C_{\text{R-azo-Na}}}{C_{\text{R-azo-Na}} + C_{\text{NaOH}}})RTc_0 \sqrt{\frac{D_{\text{eff}}t}{\pi}}$$
(3)

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**Figure 8.** Variations of the dynamic surface tensions (DST) with  $t^{1/2}$  for several concentrations of (a) *trans*-R-azo-Na solutions and (b) *cis*-rich R-azo-Na solutions at 25 °C ( $\Box$ , 0.04 mmol·L<sup>-1</sup>;  $\circ$ , 0.1 mmol·L<sup>-1</sup>;  $\Delta$ , 0.16 mmol·L<sup>-1</sup>).

Figure 8 shows the dynamic surface tensions of R-azo-Na solutions before and after UV light irradiation as a function of  $t^{1/2}$  at 0.04, 0.1, and 0.16 mmol·L<sup>-1</sup>, respectively. By linear fitting the initial adsorption process, the corresponding  $D_{eff}$  values for *trans*-R-azo-Na were estimated to be 5.64×10<sup>-11</sup>, 4.47×10<sup>-11</sup>, and 5.17×10<sup>-11</sup> m<sup>2</sup>·s<sup>-1</sup>. The corresponding  $D_{eff}$  values for the molecules in *cis*-rich R-azo-Na solutions were 4.57×10<sup>-11</sup>, 4.42×10<sup>-11</sup>, and 5.27×10<sup>-11</sup> m<sup>2</sup>·s<sup>-1</sup>, respectively. This indicates that, for the present system, the  $D_{eff}$  is almost irrespective of the surfactant concentrations below *cmc*, in considering the experimental error<sup>60</sup>. By a pulsed-field gradient NMR method, the self-diffusion coefficient *D* value of *trans*-R-azo-Na at 0.1 mmol·L<sup>-1</sup> (0.37 *cmc*) and 25 °C was measured to be 5.10×10<sup>-10</sup> m<sup>2</sup>·s<sup>-1</sup>, so was that of in *cis*-rich R-azo-Na solutions<sup>61</sup>. The  $D_{eff}$  /*D* was 0.0876 for *trans*-R-azo-Na system and 0.0867 for *cis*-rich R-azo-Na system, verifying the existence of a significant adsorption barrier for the adsorption of R-azo-Na before and after UV light irradiation<sup>60</sup>. Therefore, at the beginning of the adsorption process, the adsorption kinetics belong to a mixed diffusion-kinetic-controlled mechanism.

The energy barrier  $E_a$ , which is related to the orientation of molecules and the reconstruction of the surface<sup>62</sup>, can be expressed with  $D_{eff}$  and D by an Arrhenius-type relationship, as shown in equation (4).

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$$D_{\rm eff} = D \exp(-\frac{2E_{\rm a}}{RT}) \tag{4}$$

The  $D_{\rm eff}$  values of 0.1 mmol·L<sup>-1</sup> trans-R-azo-Na solution and cis-rich R-azo-Na solution at several temperatures were obtained by fitting their dynamic surface tension data (Supporting Information Figure S22). The self-diffusion coefficient D values at the corresponding temperatures were estimated according to the Stokes-Einstein equation<sup>63</sup>. According to the plot of  $\ln (D_{\text{eff}}/D)$  vs 1/T (Figure S23), the  $E_a$  value becomes accessible. The results show that even with the presence of extra ions<sup>60</sup> the  $E_a$  value for the adsorption of *trans*-R-azo-Na at the surface is still as large as 23.1 kJ·mol<sup>-1</sup>, which is obviously larger than that of many traditional surfactants<sup>60-61, 64</sup>. By comparing their molecular structures, it is clear that the bulkiness of the rigid skeleton of trans-R-azo-Na accounts for the high energy barrier of adsorption. This situation is similar to the Pickering foams stabilized by nanoparticles. The adsorption of nanoparticles at interfaces is almost irreversible because of the extremely high desorption energy barriers<sup>65</sup>. On the other hand, the  $E_a$  value for the adsorption process in *cis*-rich R-azo-Na solutions is 11.0 kJ·mol<sup>-1</sup>. As mentioned above, because the *trans*-R-azo-Na has a strong ability to adsorb at the interface, the air/water interface in cis-rich R-azo-Na solutions at equilibrium is in fact mainly occupied by the remaining *trans*-R-azo-Na molecules. However, at the beginning of the adsorption, part of the cis-R-azo-Na molecules may also adsorb at the interface. This mixed adsorption of both isomers resulted in a smaller E<sub>a</sub> and indicated different adsorption behavior of trans and cis R-azo-Na molecules.

#### Conclusions

Photoresponsive foams formed by a rigid azobenzene surfactant (R-azo-Na) derived from dehydroabietic acid have been investigated. Under UV light irradiation, the stable foams formed by *trans*-R-azo-Na quickly collapsed due to the *trans-cis* isomerization of the azobenzene group, showing an in situ response. The extremely high photoresponsive efficiency of the foams was attributed to the totally rigid hydrophobic skeleton of R-azo-Na, which leads to unique adsorption behavior among reported azobenzene surfactants. The results show the advantage of a totally rigid surfactant in constructing highly effective photoresponsive systems. Because of the unusual

molecular structure and dynamic behavior, a surfactant with a rigid skeleton is also expected to bring out novel properties in other related systems. The present work reveals the importance of molecular rigidity of surfactants and is also beneficial to widen the applications of rosin in new fields of technology.

**Supporting Information**. Synthesis and <sup>1</sup>H NMR spectrums of compounds, determination of water solubility, fluorescence measurements, foaming properties of *trans*-R-azo-Na and SDS, dynamic surface tensions of R-azo-Na solutions before and after UV light irradiation.

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