Title
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Permalink
https://escholarship.org/uc/item/3nq3k6m9

Journal
Langmuir, 30(1)

ISSN
0743-7463

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Publication Date
2014-01-14

DOI
10.1021/la4034782

Peer reviewed
Photoinduced Demulsification of Emulsions Using a Photoresponsive Gemini Surfactant

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Supporting Information

ABSTRACT: This Article reports on the influence of light irradiation on the stability of emulsions prepared using a photoresponsive gemini surfactant (C₇-azo-C₇) having an azobenzene skeleton as a spacer. When mixtures of trans C₇-azo-C₇ aqueous solution and n-octane are homogenized, stable emulsions are obtained in a specific region of weight fraction and surfactant concentration. Fluorescence microscopy observations using a small amount of fluorescent probes show that the stable emulsions are oil-in-water (O/W)-type. UV irradiation of stable O/W emulsions promotes the cis isomerization of trans C₇-azo-C₇ and leads to the coalescence of the oil (octane) droplets in the emulsions, that is, demulsification. While the equilibrated interfacial tension (IFT) between aqueous trans C₇-azo-C₇ solution and octane is almost the same as that between aqueous cis C₇-azo-C₇ and octane, the occupied area per molecule for C₇-azo-C₇ at octane/water interface decreases with the cis photoisomerization of trans isomer. Dynamic IFT measurement shows that UV irradiation to the interface between aqueous trans C₇-azo-C₇ solution and octane brings about an increase in the interfacial tension, indicating that the Gibbs free energy at the interface increases. From these results, the cis isomerization of trans C₇-azo-C₇ molecules at the O/W interface due to UV irradiation leads to direct contact between the water and octane phases, because of the reduction of molecular area at the interface, and subsequently makes the emulsions demulsified.

INTRODUCTION

Emulsions are metastable systems where one liquid (dispersed) is dispersed as particles in another liquid (dispersion medium). Emulsions are broadly classified into two categories of O/W (oil in water)- and W/O (water in oil)-types. In either case of O/W or W/O emulsions, preparation of emulsions leads to an increase in interfacial area of water and oil phases; thus emulsions are thermodynamically unstable and cause eventual phase separation. However, emulsions have been used in many fields, including cosmetics and paints, and much research has focused on the enhancement of emulsion stability. On the other hand, demulsification, which is a phase separation phenomenon of stable emulsions, also plays an important role in industry. For example, aqueous waste fluids containing hazardous substances can be mixed with an oil to obtain an emulsion, and then the emulsion is demulsified to extract hazardous substances into the oil phase. This process is called “emulsion liquid membrane extraction.” Demulsification has been so far performed by adding chemicals (e.g., salt) or mechanical external forces (e.g., centrifuge) and the variation of temperature. There have been a number of studies of stimuli-responsive surfactants because interfacial properties of solutions containing the surfactants can be controlled by external stimuli, such as temperature, pH variation, redox reaction. In particular, because light is comparatively easy to handle and its use generates no pollution in surfactant solutions, the use of light as an external stimulus is attractive. Azobenzene derivatives exhibit photoisomerization between trans and cis isomers. The two isomers can be reversibly switched with irradiation of particular wavelength of light; trans isomer is converted to the cis by ultraviolet (UV) light, and visible (vis) light irradiation converts cis isomer to the trans one. Recently, studies of controls over interfacial properties of aqueous solutions and morphologies of aggregates for surfactants having azobenzene groups have been reported.

In this work, we will focus on the control over the stability of emulsions by an external stimulus. Stimuli-responsive emulsions have generally contained stimuli-responsive surfactants or polymers as emulsifiers. Change in emulsion properties by

Received: September 10, 2013
Revised: November 21, 2013
Published: December 19, 2013
external stimuli influences the stability of emulsions. In the case of emulsions prepared from pH-responsive polymer particles, the addition of acids or bases causes a drastic change in emulsion stability. However, the addition of acids or bases to emulsions sometimes falls into disfavor because the addition contaminates emulsions.

When looking at thermodynamically stable systems apart from emulsions, there have been a few studies of active phase separation. Eastoe et al. have investigated photosensitive microemulsion and demonstrated that UV irradiation brought about phase separation of the microemulsions containing a photocleavable surfactant. In addition, they have succeeded in phase separation of a single-phase microemulsion consisting of decane and aqueous mixed solution of a photocleavable surfactant and AOT by UV light irradiation. Materials for synthesis of C7-azo-C7 were all purchased from Aquasol (Asahi Spectra Co., Ltd., Tokyo, Japan). Silicone oil of low viscosity (10 cSt) was purchased from Sigma-Aldrich Co. (St. Louis, MO). Pyrene and calcine (Dojindo Molecular Technologies, Inc., Tokyo, Japan) were used as oil-soluble and water-soluble fluorescent compounds, respectively. Materials for synthesis of C7-azo-C7 were all purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All materials were used as purchased.

C7-azo-C7 Synthesis. C7-azo-C7 was synthesized by the reaction with 1-iodoheptane and 4,4′-bis-[1-2-(N,N-dimethylamino)]ethoxy azobenzene, which was synthesized by the method reported in a previous paper, followed by ion exchange where counterions in the gemini surfactant are exchanged from I− to Cl−. NMR measurements were carried out at 30 °C on a Bruker Avance DPX-400 spectrometer, equipped with a QNP probe operating at 400 MHz for 1H nucleus. All samples of synthesized compounds were prepared using d6-DMSO (Acros Organics; 99.8 atom %D). 1H NMR chemical shifts were determined by a reference signal for the residual proton in d4-DMSO (DMSO: 2.50 ppm). MS measurements using the fast atom bombardment (FAB) method were performed with a JEOL JMS-SX102A.

C7-azo-C7. 4,4′-Bis-[1-2-(N,N-dimethylamino)]ethoxy azobenzene (1.06 g, 3.0 mmol) and 1-iodoheptane (1.70 g, 9.0 mmol) were dissolved in anhydrous acetonitrile (20 mL) under nitrogen gas, and the reaction mixture was heated for 60 h at 80 °C. After the reaction, the mixture was evaporated to dryness. C7-azo-C7 1H NMR (ppm, solvent d6-DMSO): δ 0.88 (6H, t, J = 5.9 Hz), 1.22–1.40 (16H, m), 1.71–1.73 (4H, m), 3.15 (12H, s), 3.36–3.41 (4H, m), 3.80 (4H, t, J = 5.7 Hz), 4.56 (4H, t, J = 5.8 Hz), 7.18 (2H, d, J = 9.0 Hz), 7.89 (2H, d, J = 8.9 Hz). HRMS (FAB+): obs 681.3605 [M − I]−, calc 681.3599 [M − I]−.

Emulsion Preparation. Aqueous surfactant solutions were prepared in high-purity H2O (Milli-Q pure water; R = 18 MΩ cm, γ = 72.8 mN m−1 at 20 °C). Binary mixtures of aqueous trans isomer of C7-azo-C7 solution and octane were homogenized for 5 min at 10 000 rpm using an AHG-160D ultraturax homogenizer (AS ONE, Osaka, Japan) equipped with a HT1010 shaft generator (AS ONE) to prepare emulsions at 25 °C. The cis isomer of C7-azo-C7 was prepared by irradiating UV light (wavelength 365 ± 15 nm) using a Handy UV Lamp SLUV-8 (AS ONE) to aqueous C7-azo-C7 solution for at least 240 min. It took at least 240 min to get the photostationary state of photoisomerization of C7-azo-C7. In the photostationary state, the ratio of cis and trans isomers was measured on the basis of NMR signals (Supporting Information Figure S1), and it was 96:4 (mol/mol). Aqueous cis C7-azo-C7 solution was provided for emulsion preparation as well as trans C7-azo-C7.

Emulsion Characterization. The stability of emulsions was evaluated by visual observation after the emulsions were stored over 1 week at 25 °C. Emulsions containing a small amount (6 μM) of fluorescent substance (6 μM of calcine in water phase or 6 μM of pyrene in octane phase) were observed by light and fluorescence microscopes. Differential interference contrast (DIC) and fluorescence microscopy observations were performed with a Leica DMI 4000B microscope (Leica Microsystems GmbH, Wetzlar, Germany) equipped with a Leica EL6000 (mercury short-arc reflector lamp, 120 W). Digital images of samples were captured using a Leica DFC300 FX digital camera. In fluorescence microscopy observations, filter cubes A (blue) and I3 (green) were used.

Light Irradiation. On a macroscopic scale, an emulsion (5.2 mL) was placed in a vial container (container volume: 10 mL, diameter × height = 2 cm × 3 cm) and then irradiated by UV or visible light in a dark room at 25 °C (Supporting Information Figure S3a). The cis isomerization of emulsions prepared using trans C7-azo-C7 was performed on a Handy UV lamp SLUV-8 (AS ONE) that emits UV light having a wavelength of 365 ± 15 nm. The lamp was laid on the side of the vial and placed 3 cm away from the vial. The intensity of irradiated light was 15 mW cm−2. Change in the emulsion with UV irradiation was recorded with a video camera (Everio G2-HM450, JVC KENWOOD, Kanagawa, Japan). Emulsions prepared with cis C7-azo-C7 were illuminated with visible light (wavelength: 400–700 nm) using a LAX-Cute (Asahi Spectra Co., Ltd., Tokyo, Japan) equipped with a 100 W Xe lamp.

On a microscopic scale, several droplets of emulsions prepared using trans C7-azo-C7 were placed on a glass slide, and subsequently UV light (wavelength: 340–380 nm, LAX-Cute) was irradiated from 3 cm above the glass slide (Supporting Information Figure S3b). The
light intensity was adjusted to 15 mW cm\(^{-2}\). Changes in the emulsion droplets with light irradiation were recorded with a Leica microscope using the software, Leica LAS MultiTime.

**Measurement of Equilibrated and Dynamic Interfacial Tensions.** Equilibrated and dynamic interfacial tensions of octane/aqueous cis C\(_7\)-azo-C\(_7\) solution were measured with the Wilhelmy plate method (platinum plate) using a KRÜSS model K12 surface tensiometer at 30 °C. Equilibrated interfacial tensions of octane/aqueous cis C\(_7\)-azo-C\(_7\) solution were measured under UV light irradiation to the interface in a dark room, whereas those for octane/aqueous trans isomer solution were measured under an ambient atmosphere at 30 °C. In the case of dynamic interfacial tension measurements, after the interface between octane (8.4 mL) and 10 mM of C\(_7\)-azo-C\(_7\) aqueous solution (10 mL) in a beaker (diameter \(\times\) height = 3 cm \(\times\) 4 cm) was equilibrated in a dark room at 30 °C, UV light (Handy UV lamp SLUV-8) was irradiated to the interface from 5 cm above the surface of octane/C\(_7\)-azo-C\(_7\) aqueous solution in the course of the measurement.

## RESULTS AND DISCUSSION

**Emulsions Consisting of Aqueous C\(_7\)-azo-C\(_7\) Solutions and Octane.** Figure 2 shows a phase diagram for the mixtures of aqueous C\(_7\)-azo-C\(_7\) solution and n-octane at various surfactant concentrations at 25 °C. The diagram shows the relationship between weight fraction \(f_w\) of trans C\(_7\)-azo-C\(_7\) aqueous solution in the mixtures and the surfactant concentration. "Stable emulsions" are stable for over a week (continuous lines). In the case that the oil and water phases separate within a week, the emulsion is recorded as an "unstable emulsion". The regions of "stable emulsions" on second, fourth, and sixth days after emulsion preparation are shown as dashed lines, dashed dotted lines, and dotted lines, respectively. No matter what the composition is, UV light irradiation makes any stable emulsions destabilize.

![Figure 2](image.png)

**Figure 2.** Phase diagram for mixtures of aqueous C\(_7\)-azo-C\(_7\) solution and n-octane at various surfactant concentrations at 25 °C. The diagram shows the relationship between weight fraction \(f_w\) of trans C\(_7\)-azo-C\(_7\) aqueous solution in the mixtures and the surfactant concentration. "Stable emulsions" are stable for over a week (continuous lines). In the case that the oil and water phases separate within a week, the emulsion is recorded as an "unstable emulsion". The regions of "stable emulsions" on second, fourth, and sixth days after emulsion preparation are shown as dashed lines, dashed dotted lines, and dotted lines, respectively. No matter what the composition is, UV light irradiation makes any stable emulsions destabilize.

Stable emulsions consisting of mixtures of octane/10 mM of aqueous trans C\(_7\)-azo-C\(_7\) solution = 70/30 (w/w) were observed using a light and fluorescence microscopes to determine the type of the emulsions. As can be seen in Figure 3, the images indicate that the continuous phase is aqueous surfactant solution because the continuous phase shows green fluorescence coming from calcein of an aqueous fluorescent compound (Figure 3d), whereas the dispersed droplets exhibit blue fluorescence coming from pyrene (Figure 3b), which is soluble in octane. Therefore, the binary mixtures of octane/aqueous trans C\(_7\)-azo-C\(_7\) solution = 70/30 (w/w) are O/W-type emulsions.

![Figure 3](image.png)

**Figure 3.** Light and fluorescence microscopy images of stable emulsions of binary mixtures consisting of aqueous trans-isomer of C\(_7\)-azo-C\(_7\) solution and n-octane containing pyrene ((a) and (b)) or calcein ((c) and (d)). All scale bars are 30 μm.

Figure 4 is the number distribution of diameters of oil droplets (octane phase) dispersed in emulsions consisting of octane and 10 mM of C\(_7\)-azo-C\(_7\) aqueous solution (octane/aqueous surfactant solution = 70/30 (w/w)).

![Figure 4](image.png)

**Figure 4.** Number distribution of diameters of oil droplets in emulsions consisting of octane and 10 mM of C\(_7\)-azo-C\(_7\) aqueous solution (octane/aqueous surfactant solution = 70/30 (w/w)). The measurement was performed by observing 457 oil droplets through the light microscope. The number-averaged diameter is 8.9 ± 3.9 μm.

**Influence of Light Irradiation on Emulsions.** As described above, O/W emulsions were prepared in a specific weight fraction and surfactant concentration. UV light was irradiated to stable emulsions consisting of octane/10 mM of aqueous trans C\(_7\)-azo-C\(_7\) solution = 70/30 (w/w). The measurement was performed by observing 457 oil droplets through the light microscope. The number-averaged diameter is 8.9 ± 3.9 μm. UV light irradiation after about 6 h (Figure 5c) (see also movie S1, Supporting Information). The UV light irradiation causes photoisomerization from trans to cis C\(_7\)-azo-C\(_7\) in the emulsions.
emulsions containing trans C_{7}-azo-C_{7} molecules drastically decreases with UV light irradiation. Stabilities of emulsions prepared with ionic surfactants depend on the viscosities of the emulsions, van der Waals attractions, and/or electrostatic repulsions between dispersed droplets. The stability of emulsions prepared from aqueous cis isomer of C_{7}-azo-C_{7} solution and octane has been investigated. The cis isomer of C_{7}-azo-C_{7} was prepared with UV light irradiation to aqueous trans C_{7}-azo-C_{7} solutions having a concentration of 10 mM. The UV light irradiation of more than 240 min leads to photostationary states of the cis isomer of C_{7}-azo-C_{7}. In the photostationary states, the molar ratio of cis and trans isomers in 10 mM of C_{7}-azo-C_{7} solutions is 96:4. When the mixtures of octane/10 mM of aqueous C_{7}-azo-C_{7} solution, with 96 mol % of C_{7}-azo-C_{7} cis isomers (=70/30, w/w), are homogenized, emulsions are obtained without phase separation (Figure 5d). When visible light is irradiated to the emulsions, there is no change in the stability of emulsions. Therefore, these results indicate that the demulsification is caused in the process of photoisomerization from trans to cis isomer in O/W emulsions.

Figure 7 shows the equilibrated interfacial tensions (IFTs) between octane and aqueous C_{7}-azo-C_{7} solutions versus the surfactant concentration. Both IFTs for trans and cis isomers decrease with increasing surfactant concentration and reach a constant value above a specific concentration. Regarding the minimum IFT values for trans and cis isomers, there is little difference between them. As a result, the equilibrated IFT values seem not to be a trigger for the photoinduced demulsification. On the other hand, because trans and cis C_{7}-azo-C_{7} molecules are insoluble in octane, the occupied areas per molecule (A) for trans and cis C_{7}-azo-C_{7} at octane/water interface are calculated using the Gibbs’s absorption isotherm and the slope of the IFT versus the surfactant concentration. The A values for trans and cis C_{7}-azo-C_{7} molecules are 3.2 and 1.6 nm$^2$, respectively. UV light irradiation brings about a decrease in the occupied areas per molecule at octane/water interface. This is consistent with photoinduced behavior reported in a previous paper, which reports a decrease in molecular area for an anionic gemini surfactant having a stilbene as a spacer at the air/water with trans—cis photoisomerization. Although an azobenzene skeleton in C_{7}-azo-C_{7} molecule is rigid, photoisomerization from trans to cis isomer
will make the azobenzene group bent. The distance between para carbon atoms (4- and 4′-carbons) in azobenzene decreases from ca. 0.90 nm in the trans isomer to 0.55 nm in the cis isomer by trans–cis photoisomerization. Thus, a decrease in the length of azobenzene spacer in C7-azo-C7 molecule with UV light irradiation will lead to decrease in the occupied areas per molecule at the octane/water interface.

Figure 8 shows the dynamic IFTs between octane and 10 mM of aqueous C7-azo-C7 solutions as a function of time (t).

![Figure 8. Change in the interfacial tension (IFT) of n-octane/10 mM aqueous C7-azo-C7 solution systems by UV light irradiation. There is no change in the IFT before UV light irradiation in the range of t < 220 s, indicating that trans C7-azo-C7 molecules reached the adsorption equilibrium at the n-octane/water interface. UV light irradiation starts at t = 220 s, and the IFT drastically increases to a maximum value at t = 310 s, indicating that the Gibbs free energy at the interface increases. Finally, the IFT gradually decreases with irradiation time of UV light, and the value reaches the equilibrated IFT of cis-isomer.](Image)

Before UV light irradiation (t < 220 s), the IFT is constant, indicating that the adsorption of trans C7-azo-C7 molecules at the octane/water interface is equilibrated. When the interface is exposed to UV light at t = 220 s, the IFT abruptly increases by 0.6 mN m⁻¹ from 10.5 to 11.1 mN m⁻¹. The IFT increases to t = 310 s, and then gradually decreases with increasing irradiation time. The value reaches an equilibrated IFT value (9.7 mN m⁻¹) of cis C7-azo-C7 after more than 1580 s of irradiation. The abrupt increase in the dynamic IFT with UV light irradiation indicates that the Gibbs free energy at the interface increases. This results from a reduction of the occupied areas per C7-azo-C7 molecule at the octane/water interface with trans–cis photoisomerization, followed by temporal and partial exposures (direct contact) of octane and water phases at the interface, contributing to an increase in the IFT. The cis isomers of C7-azo-C7 molecules generated by UV light irradiation seek their equilibrium state at the interface. As a result, a temporal increase in IFT is observed in the initial time of the irradiation (220 < t < 310 in Figure 8).

Considering the results of the equilibrated and dynamic IFT measurements, we suggest the following mechanism for the photoinduced demulsification described above. When UV light is exposed to an stable emulsion consisting of octane and water containing 10 mM of a Gemini surfactant having no azobenzene group (1,2-bis(dodecyl(dimethylammonium)ethane dibromide) for 6 h, no phase separation is observed (Figure 9a,b). In addition, octane containing 10 mM of azobenzene and 20 mM of aqueous sodium dodecyl sulfate (SDS) solution was mixed (octane/aqueous solution = 70/30, w/w) and homogenized to obtain stable emulsions (Figure 9c). After UV light is irradiated to the stable emulsion for 6 h, the emulsion remains the same (Figure 9d). Thus, an azobenzene group of a spacer in C7-azo-C7 plays an important role in the solution (see Figure 8), indicating that direct contact between octane and water phases is temporally (Scheme 1b). The exposures of octane/water interface bring about the coalescence of octane droplets in O/W-type emulsions to reduce the interfacial Gibbs free energy, followed by the complete phase separation, demulsification (Scheme 1c). For emulsions formed from the mixture of octane and 10 mM of aqueous C7-azo-C7 solution having a weight ratio of 70:30, the number-averaged diameter of octane droplets was 8.9 μm as seen in Figure 4. Assuming the density of octane to be 0.702 g mL⁻¹, there exist 2.7 × 10⁶ of octane droplets in 10 g of emulsion, and thus the emulsion has 6.7 m² of interfacial area. The increase in the interfacial tension by 0.6 mN m⁻¹ upon trans–cis isomerization, as seen in Figure 8, corresponds to an increase in the interfacial Gibbs free energy by 4.0 mJ in the emulsion, and therefore the emulsion will cause coalescence of octane droplets to decrease interfacial area in the emulsion, followed by a decrease in the free energy. Light microscopy observations confirm the above-mentioned mechanism (see Supporting Information movie S2). More specifically, the octane droplets coalesce intermittently with the trans–cis photoisomerization until the octane and water phases are fully separated.

Additional experiments were done to confirm the mechanism of photoinduced demulsification described above. When UV light is exposed to an stable emulsion consisting of octane and water containing 10 mM of a Gemini surfactant having no azobenzene group (1,2-bis(dodecyl(dimethylammonium)ethane dibromide) for 6 h, no phase separation is observed (Figure 9a,b). In addition, octane containing 10 mM of azobenzene and 20 mM of aqueous sodium dodecyl sulfate (SDS) solution was mixed (octane/aqueous solution = 70/30, w/w) and homogenized to obtain stable emulsions (Figure 9c). After UV light is irradiated to the stable emulsion for 6 h, the emulsion remains the same (Figure 9d). Thus, an azobenzene group of a spacer in C7-azo-C7 plays an important role in the

![Scheme 1. Possible Mechanism of Demulsification with UV Light Irradiation](Image)
photoinduced demulsification. These results will support the aforementioned mechanism of photoinduced demulsification.

To generalize the mechanism, we tried photoinduced demulsification of emulsions consisting of 10 mM aqueous C<sub>7</sub>-azo-C<sub>7</sub> solutions and other oils (methyl decanoate, 1-nonanol, and silicon oil). If the mechanism of photoinduced demulsification is correct, UV light irradiation should lead to the demulsification regardless of the type of oils. When mixtures of methyl decanoate or 1-nonanol/10 mM of aqueous trans C<sub>7</sub>-azo-C<sub>7</sub> solution (=70/30, w/w) are homogenized, O/W-type stable emulsions are obtained, and these emulsions are demulsified by UV light irradiation. When UV light is exposed to O/W-type emulsions prepared from mixtures of silicone oil/10 mM of aqueous trans C<sub>7</sub>-azo-C<sub>7</sub> solution (=80/20, w/w), the demulsification occurs by UV light irradiation. These results support that the photoinduced reduction of molecular area for C<sub>7</sub>-azo-C<sub>7</sub> at the interface of oil/water brings about coalescence of oil droplets in emulsions, and thus the oil and water phases are separated.

### CONCLUSION

We have investigated the influence of light irradiation on the emulsification property of a photoresponsive gemini surfactant, C<sub>7</sub>-azo-C<sub>7</sub>. Emulsions prepared from octane and aqueous trans C<sub>7</sub>-azo-C<sub>7</sub> solution were stable over a week and were found to be of O/W-type. UV light irradiation of the stable O/W emulsions promoted photoisomerization of trans to cis isomer and led to demulsification on the basis of coalescence of the oil droplets caused by a reduction of molecular area of the gemini surfactant at the O/W interface. An azobenzene skeleton of a spacer in the gemini surfactant plays an important role in the photoinduced demulsification.

### ASSOCIATED CONTENT

#### Supporting Information

Movies of the photoinduced demulsification upon UV light irradiation on macroscopic and microscopic scales (movies S1 and S2);<sup>1</sup> 1H NMR spectra for 10 mM of C<sub>7</sub>-azo-C<sub>7</sub> solutions in D<sub>2</sub>O before and after UV light irradiation (Figure S1); change in interfacial tensions between n-octane/10 mM of aqueous C<sub>7</sub>-azo-C<sub>7</sub> solution against UV light irradiation time measured by the pendant drop method (Figure S2); and geometries for UV light irradiation to emulsions on macroscopic and microscopic scales (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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