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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 (C_7 -azo- C_7) having an azobenzene skeleton as a spacer. When mixtures of *trans* C_7 -azo- C_7 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* C_7 -azo- C_7 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* C_7 -azo- C_7 solution and octane is almost the same as that between aqueous *cis* C_7 -azo- C_7 and octane, the occupied area per molecule for C_7 -azo- C_7 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* C_7 -azo- C_7 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* C_7 -azo- C_7 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”.^{1,2} Demulsification has been so far performed by adding chemicals (e.g., salt^{3–5} and demulsifiers^{6–8}) or by physical techniques such as the application of high electrical fields,^{9,10} or mechanical external forces (e.g., centrifuge,^{11–13} microwave^{14–16}) and the variation of temperature.^{15,17,18}

There have been a number of studies of stimuli-responsive surfactants^{19,20} because interfacial properties of solutions containing the surfactants can be controlled by external stimuli, such as temperature,^{21–23} pH variation,^{23–25} and redox reaction.^{26–28} 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.²⁹ Recently, studies of controls over interfacial properties of aqueous solutions^{30–32} and morphologies of aggregates^{33–37} 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 emulsification properties by

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external stimuli influences the stability of emulsions. In the case of emulsions prepared from pH-responsive polymer particles^{38–42} or chitosan,⁴³ 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 microemulsion⁴⁴ and demonstrated that UV irradiation brought about phase separation of the microemulsions containing a photocleavable surfactant.^{45–47} In addition, they have succeeded in phase separation of a single-phase microemulsion consisting of decane and aqueous mixed solution of a photoresponsive surfactant and AOT by UV light irradiation.⁴⁸ However, to the best of our knowledge, there are no reports concerning drastic changes in the stability of emulsions, that is, active demulsification with light irradiation.

In this Article, we report the influence of light irradiation on emulsions prepared with a photoresponsive gemini surfactant (C_7 -azo- C_7 ; see Figure 1) having an azobenzene skeleton as a

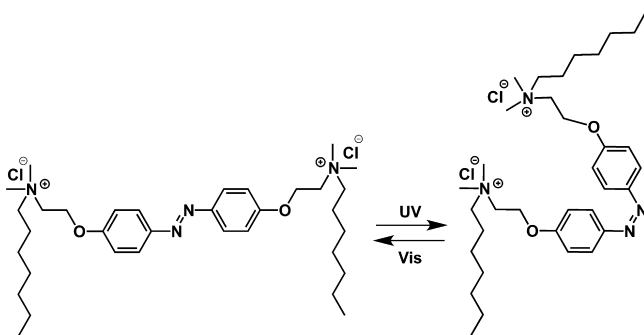


Figure 1. Chemical structures of *trans* and *cis* isomers of C_7 -azo- C_7 .

spacer. We study phase separation of stable emulsions prepared from aqueous *trans* C_7 -azo- C_7 solution and *n*-octane by UV light irradiation. We suggest that the azobenzene groups in C_7 -azo- C_7 molecules play an important role in demulsification; the geometric structure of the azobenzene group in the surfactant at the octane/water interface transforms from the *trans* form to the *cis* form with UV light irradiation and thereby causes demulsification.

EXPERIMENTAL SECTION

Materials. *n*-Octane (reagent grade, 99.8%) was purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). Methyl decanoate and 1-nonanol were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Silicone oil of low viscosity (10 cSt) was purchased from Sigma-Aldrich Co. (St. Louis, MO). Pyrene and calcein (Dojindo Molecular Technologies, Inc., Tokyo, Japan) were used as oil-soluble and water-soluble fluorescent compounds, respectively. Materials for synthesis of C_7 -azo- C_7 were all purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All materials were used as purchased.

C_7 -azo- C_7 Synthesis. C_7 -azo- C_7 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,⁴⁹ 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 d_6 -DMSO (Acros Organics; 99.8 atom %D). 1H NMR chemical shifts were

determined by a reference signal for the residual proton in d_6 -DMSO (DMSO: 2.50 ppm).⁵⁰ MS measurements using the fast atom bombardment (FAB) method were performed with a JEOL JMS-SX102A.

C_7 -azo- C_7 I^- . 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. C_7 -azo- C_7 I^- was obtained by double recrystallization from ethyl acetate (2.06 g, 85%). 1H NMR (ppm, solvent d_6 -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 [$M - I$]⁺, calcd 681.3599 [$M - I$]⁺.

C_7 -azo- C_7 . Methanol solution of C_7 -azo- C_7 I^- (2.06 g, 2.55 mmol) was passed through a column packed with an ion-exchange resin (Amberlite IRA900J Cl form, Organo Co., Tokyo, Japan). The eluted solution was evaporated to dryness to obtain the crude product. C_7 -azo- C_7 was recrystallized from ethyl acetate and obtained as a yellow solid (1.56 g, 98%). 1H NMR (ppm, solvent d_6 -DMSO): δ 0.88 (6H, t, J = 5.8 Hz), 1.21–1.38 (16H, m), 1.71–1.73 (4H, m), 3.15 (12H, s), 3.36–3.42 (4H, m), 3.80 (4H, t, J = 5.8 Hz), 4.56 (4H, t, J = 5.8 Hz), 7.18 (2H, d, J = 9.0 Hz), 7.89 (2H, d, J = 9.0 Hz). HRMS (FAB+): obs 589.4246 [$M - Cl$]⁺, calcd 589.4243 [$M - Cl$]⁺.

Emulsion Preparation. Aqueous surfactant solutions were prepared in high-purity H_2O (Milli-Q pure water; $R = 18$ M Ω cm, $\gamma = 72.8$ mN m⁻¹ at 20 °C). Binary mixtures of aqueous *trans* isomer of C_7 -azo- C_7 solution and octane were homogenized for 5 min at 10 000 rpm using an AHG-160D ultrafast homogenizer (AS ONE, Osaka, Japan) equipped with a HT1010 shaft generator (AS ONE) to prepare emulsions at 25 °C. The *cis* isomer of C_7 -azo- C_7 was prepared by irradiating UV light (wavelength 365 ± 15 nm) using a Handy UV Lamp SLUV-8 (AS ONE) to aqueous C_7 -azo- C_7 solution for at least 240 min. It took at least 240 min to get the photostationary state of photoisomerization of C_7 -azo- C_7 . 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* C_7 -azo- C_7 solution was provided for emulsion preparation as well as *trans* C_7 -azo- C_7 .

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 μ M) of fluorescent substance (6 μ M of calcein in water phase or 6 μ M 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 \times height = 2 cm \times 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* C_7 -azo- C_7 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 GZ-HM450, JVC KENWOOD, Kanagawa, Japan). Emulsions prepared with *cis* C_7 -azo- C_7 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* C_7 -azo- C_7 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 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

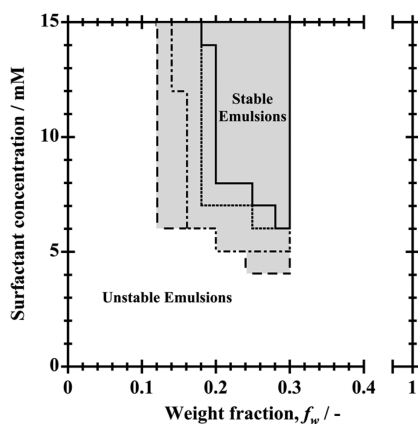


Figure 2. Phase diagram for mixtures of aqueous C_7 -azo- C_7 solution and *n*-octane at various surfactant concentrations at 25°C . The diagram shows the relationship between weight fraction (f_w) of *trans* C_7 -azo- C_7 aqueous solution in the mixtures and the surfactant concentration. “Stable emulsions” 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.

of aqueous *trans* C_7 -azo- C_7 solution and octane at 25°C . Emulsions that give no phase separation over 1 week after preparation were evaluated as “stable emulsions”. Stable emulsions were obtained in a specific region in the phase diagram. The weight fractions (f_w) of aqueous *trans* C_7 -azo- C_7 solution and the surfactant concentration to exhibit stable emulsions were $0.2 \leq f_w \leq 0.3$ and over 6 mM, respectively.

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

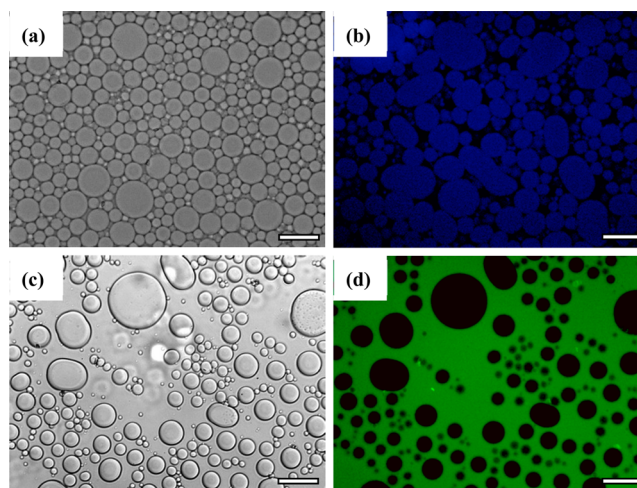


Figure 3. Light and fluorescence microscopy images of stable emulsions of binary mixtures consisting of aqueous *trans*-isomer of C_7 -azo- C_7 solution and *n*-octane containing pyrene ((a) and (b)) or calcein ((c) and (d)). All scale bars are $30 \mu\text{m}$.

soluble in octane. Therefore, the binary mixtures of octane/ aqueous *trans* C_7 -azo- C_7 solution are O/W-type emulsions.

Figure 4 is the number distribution of diameters of oil droplets (octane phase) dispersed in emulsions consisting of

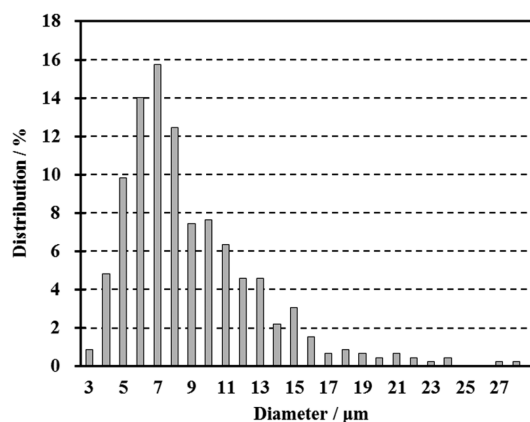


Figure 4. Number distribution of diameters of oil droplets in emulsions consisting of octane and 10 mM of C_7 -azo- C_7 aqueous solution (octane/ aqueous surfactant solution = 70/30 (w/w)).

octane and 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 $8.9 \pm 3.9 \mu\text{m}$.

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). Figure 5 shows the change in the emulsions after UV light irradiation in a dark room. When UV light is irradiated to stable O/W emulsions, octane and aqueous C_7 -azo- C_7 solution phases are gradually separated from the emulsions, that is, the process of demulsification. These phases are completely separated by 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

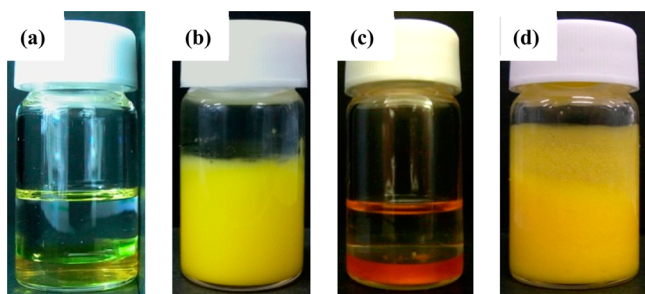


Figure 5. Photographs illustrating the demulsification of a stable emulsion consisting of *n*-octane/aqueous C_7 -azo- C_7 solution at 10 mM (=70/30, w/w): (a) binary mixture of octane and aqueous C_7 -azo- C_7 solution before homogenization, (b) after homogenization, and (c) macroscopic demulsification caused by UV light irradiation to the emulsion shown in (b). (d) Emulsion consisting of *n*-octane and the aqueous *cis*-isomer of C_7 -azo- C_7 solution (no phase separation).

because the color of aqueous C_7 -azo- C_7 solutions after UV light irradiation changes from yellow to red corresponding to *cis* isomer as shown in Figure 5c. In contrast, no phase separation is observed when UV light is not irradiated to stable O/W emulsions in a dark room (movie S1, Supporting Information). Therefore, UV light irradiation to the emulsions promotes to *cis* isomerization of *trans*- C_7 -azo- C_7 molecules, leading to the phase separation.

In general, demulsification of O/W emulsions results mainly from the flocculation and coalescence of the oil droplets in emulsions and creaming caused by the density difference between oil and water phases. When the stable O/W emulsions are observed by light microscopy under UV light irradiation, the coalescence of the oil droplets (octane phase) in the emulsion is observed (Figure 6) (see also movie S2, Supporting Information). As seen in Figure 6, UV light irradiation brings about the coalescence of the oil droplets in stable O/W emulsions, and subsequently the octane and water phases separate.

Possible Mechanisms of Demulsification by UV Light Irradiation. We discuss here why the stability of O/W

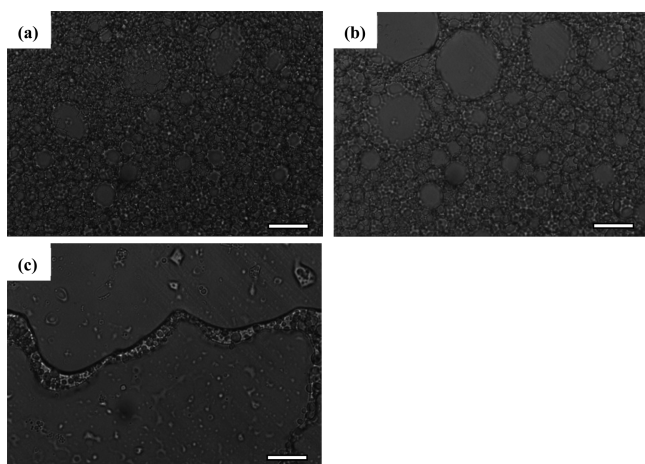


Figure 6. Light microscopy images of a stable O/W emulsion consisting of *n*-octane/aqueous *trans* C_7 -azo- C_7 solution at 10 mM (=70/30, w/w) at 25 °C: (a) before UV irradiation, (b) 40 s after UV irradiation, and (c) 60 s after UV light irradiation. The oil droplets coalesce into large ones with UV light irradiation, and then the oil and water phases separate on a microscopic scale. All scale bars are 30 μ m.

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.⁵¹ 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

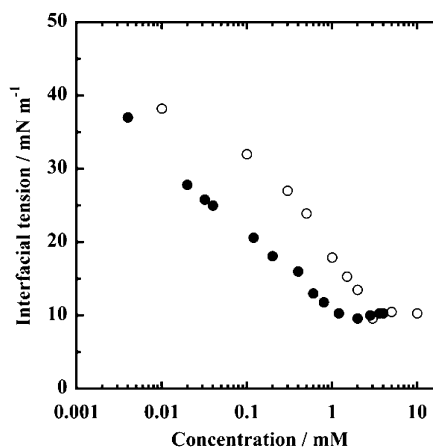


Figure 7. Interfacial tension of *n*-octane/aqueous C_7 -azo- C_7 solution systems against the surfactant concentration. ●, *trans* isomer; ○, *cis* isomer.

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 adsorption isotherm and the slope of the IFT versus the surfactant concentration.⁵² The *A* values for *trans* and *cis* C_7 -azo- C_7 molecules are 3.2 and 1.6 nm², 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,⁵³ 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.⁵⁴ Thus, a decrease in the length of azobenzene spacer in C_7 -azo- C_7 molecule with UV light irradiation will lead to the 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 C_7 -azo- C_7 solutions as a function of time (t).

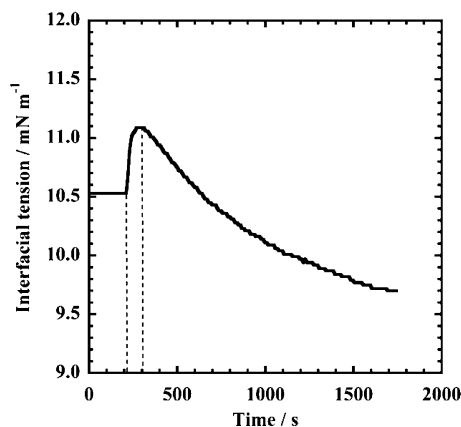
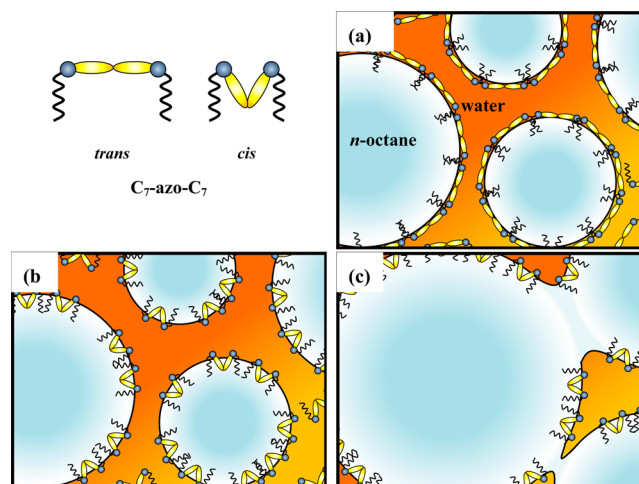


Figure 8. Change in the interfacial tension (IFT) of *n*-octane/10 mM aqueous C_7 -azo- C_7 solution systems by UV light irradiation. There is no change in the IFT before UV light irradiation in the range of $t < 220$ s, indicating that *trans* C_7 -azo- C_7 molecules reached the adsorption equilibrium 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.

Before UV light irradiation ($t < 220$ s), the IFT is constant, indicating that the adsorption of *trans* C_7 -azo- C_7 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* C_7 -azo- C_7 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 C_7 -azo- C_7 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 C_7 -azo- C_7 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 of stable O/W emulsions prepared with C_7 -azo- C_7 . As shown in Scheme 1a, *trans* C_7 -azo- C_7 molecules are adsorbed on the entire interface of octane and aqueous surfactant solution in the stable emulsions. UV light irradiation leads to a reduction of molecular area with *trans*–*cis* photoisomerization and temporal increase in the dynamic IFT at the interface of the octane/aqueous surfactant

Scheme 1. Possible Mechanism of Demulsification with UV Light Irradiation^a



^aThe *trans* C_7 -azo- C_7 molecules are adsorbed on the whole interface of *n*-octane and aqueous surfactant solution in the stable O/W-type emulsions. UV light irradiation leads to partially direct contact between water and *n*-octane phases. The exposure of the *n*-octane/water interface brings about the coalescence of the *n*-octane droplets in the O/W-type emulsions. Finally, the *n*-octane and water phases are fully separated on a macroscopic scale.

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 C_7 -azo- C_7 solution having a weight ratio of 70:30, the number-averaged diameter of octane droplets was $8.9 \mu\text{m}$ as seen in Figure 4. Assuming the density of octane to be 0.702 g mL^{-1} , there exist 2.7×10^6 of octane droplets in 10 g of emulsion, and thus the emulsion has 6.7 m^2 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 a stable emulsion consisting of octane and water containing 10 mM of a gemini surfactant having no azobenzene group (1,2-bis(dodecyltrimethylammonium)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 C_7 -azo- C_7 plays an important role in the

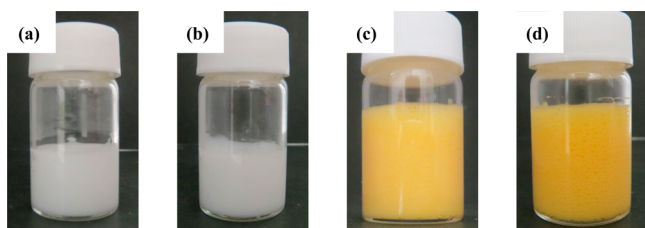


Figure 9. Emulsions consisting of *n*-octane/aqueous surfactant solution (=70/30, w/w) before and after UV light irradiation: (a) emulsion stabilized by 10 mM of 1,2-bis(dodecyldimethylammonium)-ethane dibromide containing no azobenzene group before UV light irradiation, and (b) after UV light irradiation; (c) emulsion consisting of *n*-octane containing 10 mM of azobenzene and 20 mM of aqueous SDS solution before UV light irradiation, and (d) after UV light irradiation.

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_7 -azo- C_7 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_7 -azo- C_7 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_7 -azo- C_7 solution (=80/20, w/w), the demulsification occurs by UV light irradiation. These results support that the photoinduced reduction of molecular area for C_7 -azo- C_7 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_7 -azo- C_7 . Emulsions prepared from octane and aqueous *trans* C_7 -azo- C_7 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); ^1H NMR spectra for 10 mM of C_7 -azo- C_7 solutions in D_2O before and after UV light irradiation (Figure S1); change in interfacial tensions between *n*-octane/10 mM of aqueous C_7 -azo- C_7 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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Notes

The authors declare no competing financial interest.

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