

Photochemical Control of Viscosity Using Sodium Cinnamate as a Photoswitchable Molecule

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(Received November 5, 2011; CL-111081; E-mail: hisakai@rs.noda.tus.ac.jp)

We investigated the formation of a high-viscosity wormlike-micelle solution consisting of a mixed aqueous solution containing the cationic surfactant cetyltrimethylammonium bromide (CTAB) and sodium cinnamate (NaCin) and control of the solution viscosity by photoisomerization of the NaCin. The aqueous CTAB/NaCin solution exhibited higher zero-shear viscosity than a classic wormlike micelle-forming system CTAB/sodium salicylate of the same concentration. UV irradiation of the aqueous CTAB/NaCin wormlike-micelle solution resulted in a remarkable decrease in its viscosity, from 6.6×10 to 2.1×10^{-3} Pa·s.

Interest has rapidly grown in recent years in the use of external stimuli to control the construction and deconstruction of micelles, vesicles, and other molecular aggregates formed by surfactants containing intramolecular stimulus-responsive moieties, by photochemical reactions,^{1–3} pH changes,^{4,5} and electrical stimulation (redox reactions).^{6,7} By switching between alternative forms of the molecular aggregates, it is then possible to control the solubility, viscosity, vapor pressure, and other properties of low-solubility substances.

It has also been noted that the aqueous solutions containing wormlike micelles formed by surfactants exhibit high viscoelasticity, due to their three-dimensional entanglement. Typical examples are mixed systems of cetyltrimethylammonium bromide (CTAB)/sodium salicylate (NaSal)⁸ and mixed systems of nonionic surfactants.⁹ If the construction and deconstruction of the wormlike micelles, and thus the solution viscosity, can be effectively controlled by external stimulation, it may lead to applications for controlled release of fragrances, flavors, and drugs incorporated into the micelles and for prevention of printer ink bleeding.¹⁰ Studies at our group have successfully led to light-controlled reversible viscosity changes in mixed aqueous solutions known to form micelles, consisting of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) together with a photoresponsive azobenzene-modified surfactant (4-alkylazobenzene-4'-(oxyethyl)-trimethylammonium bromide; AZTMA).¹¹ Further advantages may be obtained, however, if the organic salt added to induce micelle formation is itself photoresponsive. This would result in a simpler system that might exhibit higher efficiency for light-induced viscosity changes. Among the various known photoresponsive molecules, cinnamic acid is similar in structure to NaSal and, unlike AZTMA, requires no complex process for its synthesis. Its derivatives are already widely used as UVB region sunscreen agents.¹² In the present study, we, therefore, investigated the formation of high-viscosity micelle solutions, consisting of aqueous CTAB solutions containing sodium cinnamate (NaCin), a cinnamic acid salt and the control of their viscosity by light.

CTAB (Sigma-Aldrich Co.) was purchased and used as the cationic surfactant, and NaCin was prepared by neutralizing cinnamic acid with aqueous sodium hydroxide. This transform NaCin was added to 50 mM aqueous CTAB solution in various concentrations, and the resulting solutions were agitated well, left standing at a constant 25 °C for two days, and then used as samples. UV irradiation was performed with a 200-W mercury-xenon lamp (SAN-EI SUPERCURE-203S) equipped with a color filter (transmission wavelength region 260–390 nm; U-340), at an irradiation intensity of 10 mW cm^{-2} . The dynamic viscoelasticity of the aqueous surfactant solutions was measured by a stress-controlled rheometer (CSL100; Carri-Med Ltd.) at a constant temperature of 25 °C using a 4-cm-diameter cone (cone angle, 2°).

Figure 1 shows appearance of 50 mM aqueous CTAB solutions in the presence of NaCin with various concentrations. It was found that the consistency of the aqueous CTAB/NaCin solution proceeded toward a gel state with increasing addition of NaCin to a fixed concentration of 50 mM CTAB until the NaCin concentration reached approximately 50 mM, after which no readily observable change in the solution viscosity occurred. We, therefore, performed the dynamic viscoelasticity measurements using an equimolar aqueous CTAB (50 mM)/NaCin (50 mM) solution. As shown by the frequency dependence of G' (storage modulus) and G'' (loss modulus) in Figure 2, it was found that this solution exhibits viscous-body behavior ($G' < G''$) at lower frequencies and elastic-body behavior ($G' > G''$) at higher frequencies and that G' reaches and maintains a plateau in the high-frequency region whereas G'' declines from a maximum. This behavior resembles that of the Maxwell model observed for diluted polymer solutions. The zero-shear viscosity of this solution calculated from the plateau elasticity and retention time was found to be 66.0 Pa·s, which is considerably larger than that of a CTAB/NaSal system at the same concentration (55 Pa·s).

Many observations of Maxwell-model relaxation behavior have previously been reported for wormlike-micelle solutions such as CTAB/NaSal.^{9,10} In addition, we have observed molecular assemblies with wormlike morphology by cryo-

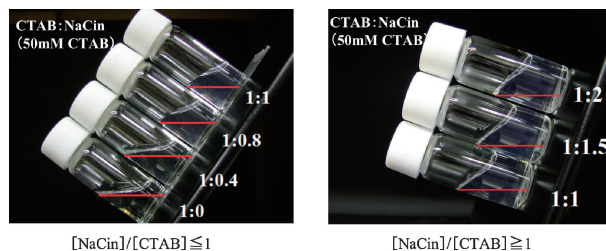


Figure 1. Visual observation of CTAB/NaCin mixed solutions.

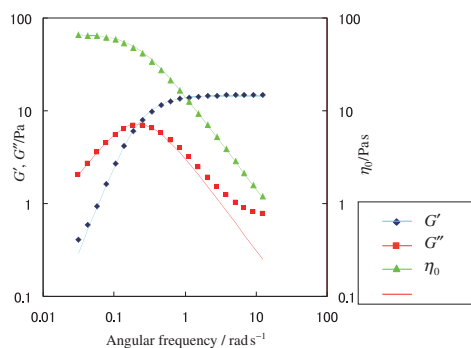


Figure 2. Dynamic viscoelasticity measurements for CTAB (50 mM)/NaCin (50 mM) solution. G' : Storage modulus, G'' : Loss modulus, η_0 : Zero shear viscosity.

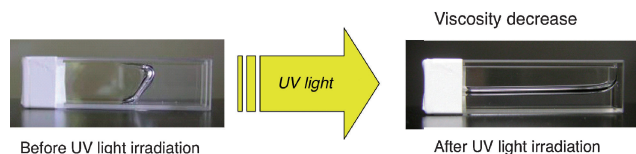


Figure 3. Viscosity decrease observed by UV light irradiation to the CTAB (50 mM)/NaCin (50 mM) solution.

TEM observation of the CTAB/NaCin solution (see Supporting Information; SI¹³). The above results confirm that wormlike micelles form in the aqueous CTAB/NaCin solution.

We next performed UV irradiation of the aqueous CTAB/NaCin solution (50 mM/50 mM) and observed it for changes in viscosity. As can be seen in Figure 3, it was found that the gel-form solution samples changed to liquid form under the irradiation, and it was thus found possible to control the viscosity of this system by UV irradiation. In measurements of its UV-vis absorption before and after the photoirradiation, the trans-form solution before UV irradiation exhibited a maximum absorption wavelength λ_{max} of 269 nm, but the absorbance was reduced by UV irradiation and the position of maximum absorption shifted to shorter wavelength (255 nm) (see SI¹³). This finding indicates that the NaCin molecules underwent photoisomerization during the irradiation, thus changing from the trans form to the cis form. The irradiation time required to reach the photostationary state was rather long, at 15–20 h, but this may be attributable to impeded light penetration to the interior regions of the samples due to their large thickness.

We next investigated the rheological behavior of the solution following UV irradiation and found that the G' and G'' frequency dependence curves gradually shifted toward higher frequency. We also found that the zero-shear viscosity fell sharply with UV irradiation. It was difficult to measure the dynamic viscoelasticity of the solution in the photostationary state, but in its rheological behavior the solution exhibited Newtonian flow, as determined by flow-curve measurements, and a solution viscosity of 2.1×10^{-3} Pa.s. This extremely small value was approximately 1/30000 of the zero-shear viscosity before UV irradiation and represents a reduction far larger than that (approximately 1/1000) of the aqueous CTAB/NaSal/AZTMA mixed solutions previously observed by us.¹¹ Figure 4 shows the results of our investigation of the change in viscosity

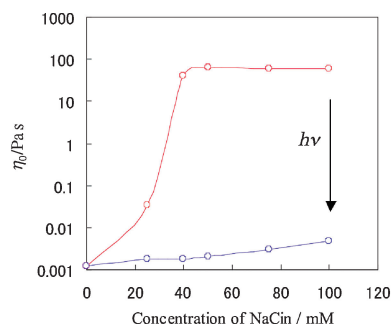


Figure 4. Zero shear viscosity of CTAB (50 mM)/NaCin solutions as a function of NaCin concentration before and after UV light irradiation.

under UV irradiation for systems containing NaCin at different concentrations with a fixed CTAB concentration. As shown, we observed a remarkable decrease in viscosity by UV irradiation in the aqueous solutions containing NaCin at concentrations of 40–100 mM.

The results of the rheological measurements suggest that the wormlike micelles were gradually changed to small molecular aggregates without entanglement by the irradiation, resulting in decreased viscosity. Moreover, when we investigated the environment of the NaCin molecules by ¹H NMR measurements before and after UV irradiation, the results suggested that in its transformation to the cis form, the carboxylic acid moiety of the NaCin becomes positioned in a more hydrophilic environment. From the results of these investigations, we surmise that the change in viscosity under irradiation involves two mechanisms: 1) photoisomerization of the NaCin molecules solubilized within the CTAB micelles induces the formation of the bulky cis form and a corresponding increase in the distance between the polar CTA⁺ groups; and 2) some of the *cis*-Cin⁻ ions which form under the UV irradiation separate from the micelle surfaces, resulting in a transformation of the wormlike micelles to nonentangling spherical or small rod-form micelles.

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