



Fluid Dynamics and Transport Phenomena

Photorheologically reversible micelle composed of polymerizable cationic surfactant and 4-phenylazo benzoic acid[☆]

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ABSTRACT

A photorheologically reversible micelle composed of polymerizable cationic surfactant *n*-cetyl dimethylallyl ammonium chloride (CDAAC) and *trans*-4-phenylazo benzoic acid (*trans*-ACA) was prepared. The effects of molar ratio of CDAAC/*trans*-ACA, time of UV and visible light irradiation and temperature on the rheological properties of micellar system were investigated. The results show that before UV irradiation the system with an optimum CDAAC/*trans*-ACA molar ratio of 1.4 forms viscoelastic micelles at 45 °C. After 365 nm UV irradiation, the viscosities of micelle systems with different concentrations at fixed molar ratio of 1.4 are decreased by 85%–95%. The CDAAC/*trans*-ACA (14 mmol·L⁻¹/10 mmol·L⁻¹) micelle system exhibits shear thinning property and its viscosity is decreased obviously with the increases of UV irradiation time less than 1 h. The rheological process during UV irradiation for CDAAC/*trans*-ACA (14 mmol·L⁻¹/10 mmol·L⁻¹) micelle proves that viscosity, elastic modulus G' and viscous modulus G'' will reduce quickly with the UV light. Furthermore, the micelle system after 1 h UV-irradiation is able to revert to its initial high viscosity with 460 nm visible light irradiation for 4 h, and the micelle can be cycled between low and high viscosity states by repetitive UV and visible light irradiations. The UV-Vis spectra of CDAAC/*trans*-ACA micelle indicate that its photosensitive rheological properties are related closely to photoisomerization of *trans*-ACA to *cis*-ACA.

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1. Introduction

Photorheological fluids (PR fluids) as intelligent materials [1] were first discovered by Wolff *et al.* [2] in 1989. PR fluids are light-sensitive through specific wavelength causing *cis*-*trans* isomerizations, dimerizations, photocission, and polymerizations or polarity changes [3–8]. Compared to electro-rheological fluids [9] and magnetic fluids [10], PR fluids have more stable rheological properties as well as environmental safety. It has potential applications in microreactor, microscale actuators and valves [11–13]. In such applications, the use of light as a modulator can be particularly advantageous since light can be directed at a precise spot with resolution of a few micrometers [14]. It has been demonstrated impressive rheology-modulation with complex synthesized light-sensitive molecules [15–22]. It is a new trend to create PR fluids from simple and existing molecules [23]. Ketner *et al.* have [24] found that *trans*-orthomethoxycinnamic acid and cetyltrimethylammonium form irreversible light-responsive viscoelastic wormlike micelles without complex synthetic method. Irreversible counter-ions comprising

styrene group have been reported, such as para-coumaric acid [25], orthomethoxycinnamic acid [26,27], and cinnamic acid (CA) [28, 29]. Azobenzene compounds have obvious advantages in terms of the reversibility and a series of fluids based on 4-phenylazo benzoic acid (ACA) that exhibits dramatic, reversible changes in fluid viscosity are reported. Shi *et al.* have reported a photoresponsive micellar solution oleyl bis (2-hydroxyethyl) methyl ammonium chloride/ACA, a promising working fluid for district heating/cooling systems [30]. The drag reduction is advantageous during fluid transport, and efficient heat transfer mode is favored when the fluid passes through heat exchangers.

Suitable surfactants and counter-ions are the keys for photosensitive fluids. In this study, we use a polymerizable cationic surfactant *n*-cetyl dimethylallyl ammonium chloride (CDAAC) [31] and mix it with counter ion of ACA to obtain a new reversible photosensitive micellar solution with optimum mixture ratio of CDAAC/ACA at 45 °C. ACA has both *cis* and *trans* structures, and *trans*-ACA can convert to *cis*-ACA with UV irradiation and is reversed under visible light [32]. Its isomerization process will be verified by UV-Vis spectroscopy, and the rheological process of CDAAC/*trans*-ACA micelle is studied with UV irradiation to prove that viscosity, elastic modulus G' and viscous modulus G'' of this micelle system reduce quickly. These results will enrich the field of light rheological micellar solution.

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2. Experimental

2.1. Materials and sample preparation

Trans-4-phenylazo benzoic acid (*trans*-ACA) (98.0%) was purchased from J&K Scientific Ltd. and used as received. The salt solutions (*trans*-ACA-Na) were prepared by adding NaOH at a 12% molar excess relative to *trans*-ACA. The polymerizable cationic surfactant CDAAC used was synthesized as reference [31]. 26.95 g (0.1 mol) *N,N*-dimethylhexadecylamine (DMA16 $\geq 95\%$), 22.96 g (0.3 mol) allyl chloride and 49.91 g ethyl acetate were mixed in a dry flask with stirrers, and the reactive system was kept at 45 °C and refluxed for 24 h. The crude product cooled to room temperature was recrystallized four times from dehydrated acetone and filtered to obtain white powder product (CDAAC, Fig. 1), which is easily soluble in water.

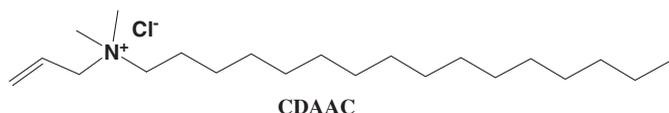


Fig. 1. Chemical structure of polymerizable cationic surfactant *n*-cetyl dimethylallyl ammonium chloride.

The CDAAC/*trans*-ACA solutions were prepared by mixing the two solutions of surfactant CDAAC and *trans*-ACA-Na. The aqueous mixtures were stirred at 45 °C for 1 h and kept in a thermostat at 45 °C for 24 h to reach equilibrium.

2.2. Characterization

2.2.1. UV and visible-irradiation

CDAAC/*trans*-ACA solutions (20 ml) were irradiated with UV light from a Spectorline UV lamp (broad band centered at 365 nm), and then followed by a 15 W LED lamp (radiation peaked at 460 nm) to irradiate samples for reversible process. To reduce the effect of atmospheric moisture, samples were placed in a sealed Petri dish (7.5 cm diameter) during the irradiation process. UV-Vis spectroscopy study before and after UV-irradiation was carried out using a SHIMADZU UV-1102 spectrophotometer.

2.2.2. Rheological measurements

Relative viscosity (η_r) was measured with a Ubbelohde viscometer (Inner diameter 0.9–1.0 mm). Steady shear viscosity (η) was measured using an Anton Paar MCR-101 rheometer at a shear rate of 200 s⁻¹ with a 25 mm cone-and-plate configuration. Shear thinning property was studied in the shear rate range from 0.1 to 100 s⁻¹. An Anton Paar MCR-702 rheometer with an inside UV lamp (broad band centered at 365 nm) was used to measure the change of steady shear viscosity and viscoelasticity during the irradiation, the steady shear rate was 200 s⁻¹, and the UV light was turned on at $t = 100$ s. In the viscoelasticity experiment, the frequency (f) was 1 Hz and the shear strain (γ) was 10%. All measurements were performed at 45 °C.

3. Results and Discussion

3.1. Effects of concentration and molar ratio

Steady shear viscosity η of CDAAC/*trans*-ACA samples at 45 °C was tested with different molar ratios of CDAAC and *trans*-ACA ([CDAAC]/[ACA]), with the *trans*-ACA concentration kept constant at 10 mmol·L⁻¹ (10 mmol·L⁻¹). At the molar ratio of CDAAC/*trans*-ACA less than 1.2, the samples present low viscosity. As CDAAC concentration increases and the molar ratio of CDAAC/*trans*-ACA reaches 1.4, η increases

obviously and reaches maximum, implying the formation and growth of wormlike micelles. However, further addition of CDAAC makes η decrease and the sample become turbid. Thus, the peak of viscosity in Fig. 2 indicates the optimum molar ratio ([CDAAC]/[ACA]) of 1.4.

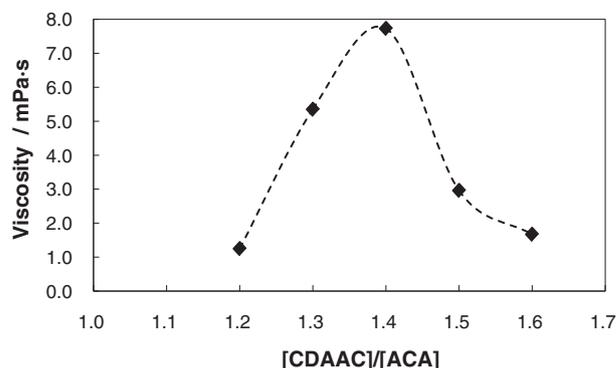


Fig. 2. Steady shear viscosity versus molar ratio ([CDAAC]/[ACA]) at *trans*-ACA concentration of 10 mmol·L⁻¹ at 45 °C.

Fig. 3 shows the photosensitivity of micelle solutions at the optimum molar ratio of CDAAC/*trans*-ACA of 1.4. With the increase of micelle concentration, the viscosity of micelle solution increases gradually. With 1 h UV irradiation, all the micelle solutions revert to low viscosity and the reduction percentage of viscosity is around 85%–95%.

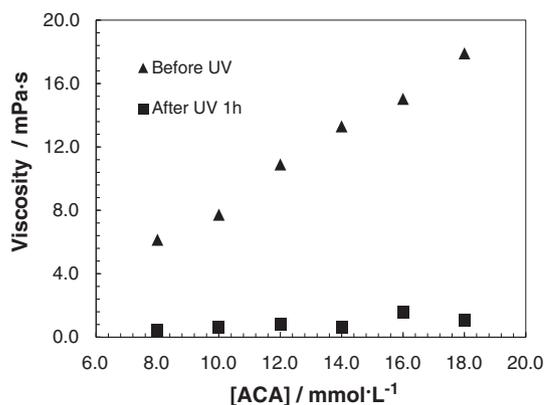


Fig. 3. Before and after UV irradiation, steady shear viscosity versus *trans*-ACA concentration ([ACA]) at molar ratio ([CDAAC]/[ACA]) of 1.4, 45 °C, and shear rate of 200 s⁻¹.

3.2. Effect of UV irradiation time on viscosity of micelle solutions

With 20 ml CDAAC/*trans*-ACA (14 mmol·L⁻¹/10 mmol·L⁻¹), viscosity curves with different UV irradiation time are showed in Fig. 4. Without irradiation, the viscosity of micelle solution keeps almost constant at low shear rate less than 1 s⁻¹, and drops significantly as shear rate increases. With the increase of UV irradiation time, the viscosity of micelle solution decreases obviously. The viscosity curve of micelle solution with 60 min UV irradiation is almost same as that with 75 min UV irradiation, and the viscosity is decreased by nearly 95% at the shear rate of 100 s⁻¹. Therefore, we consider 60 min as a suitable UV irradiation time for 20 ml CDAAC/*trans*-ACA solutions.

3.3. Rheological properties during UV irradiation process

Fig. 5 shows the photosensitivity of CDAAC/*trans*-ACA (14 mmol·L⁻¹/10 mmol·L⁻¹) solution during UV irradiation at 45 °C.

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