Colloids and Surfaces A: Physicochem. Eng. Aspects 500 (2016) 222–229

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Rheological properties and application of wormlike micelles formed by sodium oleate/benzyltrimethyl ammonium bromide

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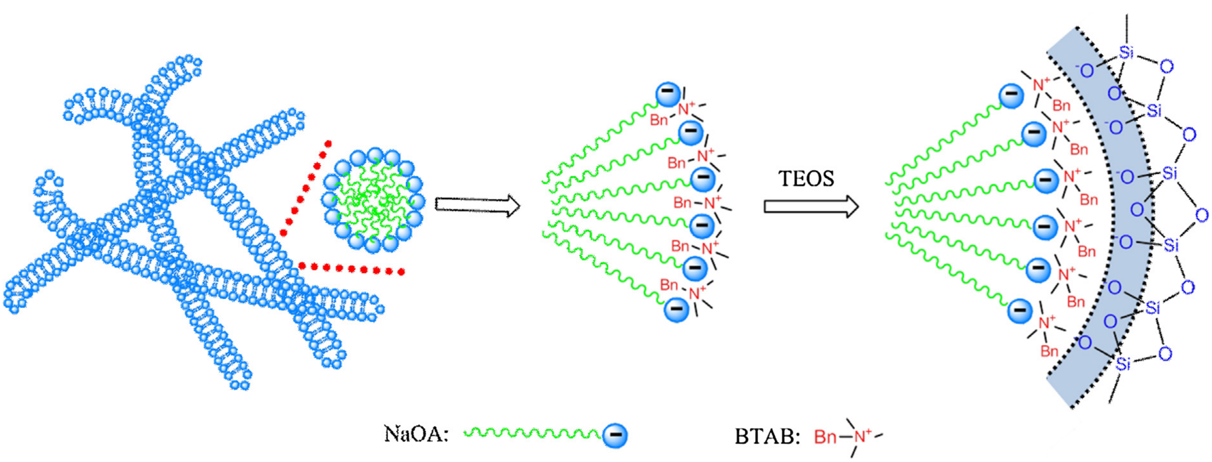
GRAPHICAL ABSTRACT



The microstructures of the wormlike micellar system can be controlled by altering the pH. The transformation between sodium oleate (NaOA) and oleic acid changes the charges on the micelle surface and affects the viscoelasticity of the system. Then, the anionic WLMs were used as templates to synthesize mesoporous silicas (MSs) whose microstructure was affected by micelle length and NaOA concentration.

HIGHLIGHTS

- A pH-responsive anionic wormlike micellar system by NaOA and BTAB.
- The anionic WLMs were used as templates to synthesize mesoporous silicas.
- Mesoporous silicas with wormhole framework.
- The mechanism explains the mesoporous formation.
- The transformation between NaOA and oleic acid affects the viscoelasticity of the system and the microstructure of MSs.

ARTICLE INFO

Article history:
Received 2 December 2015
Received in revised form 13 March 2016
Accepted 31 March 2016
Available online 31 March 2016

ABSTRACT

A pH-responsive anionic wormlike micellar (WLM) system formed by sodium oleate (NaOA) and benzyltrimethyl ammonium bromide were studied via rheological measurements and dynamic light scattering measurements. The anionic WLMs were used as templates to synthesize mesoporous silicas (MSs). The microstructures of the WLM system can be controlled by altering the pH. The transformation

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http://dx.doi.org/10.1016/j.colsurfa.2016.03.074

Keywords:
Anionic wormlike micelles
Sodium oleate
Viscoelasticity
Dynamic light scattering
Mesoporous silicas

between NaOA and oleic acid changes the charges on the micelle surface and affects the viscoelasticity of the system. High NaOA concentration increases the activation energy (E_a) of the system, whereas a high pH value promotes the formation of spherical micelles and reduces the E_a of the solutions. By contrast, a low pH value increases the viscosity of the system given that the electrostatic repulsion between NaOA head-groups is weakened. However, if numerous NaOAs transform into insoluble oleic acids, the viscosity of the system will dramatically decrease. In addition, micelle length and NaOA concentration affect the microstructure of MSs.

1. Introduction

Wormlike micelles (WLMs) are elongated and flexible aggregates formed by self-assembly of surfactant molecules [1,2]. Beyond their critical overlapping concentration, WLMs are entangled into a network and therefore the solution becomes enormously viscoelastic (reminiscent of polymer solutions) [3]. Owing to their striking rheological properties, WLMs have become important in a wide range of industrial applications, such as fracturing fluids in oil industry, as thickener in personal care products, and used for drag reduction in heat-transfer fluids [4]. A considerable amount of attention has been recently devoted to switchable WLMs, which can be reversibly tuned upon being triggered by external stimuli, such as light [5], electricity [6], pH [7], temperature [8], and metal ion [9].

Compared with other external stimuli, pH is a parameter that can be applied to control viscoelastic fluids. Two strategies are generally used to form pH-switchable WLM systems. The more common route is the direct use of pH-sensitive surfactants to formulate WLMs [7,10]. Zhang et al. [7] demonstrated that erucic acid alone can be used to develop pH-switchable WLMs, which can be reversibly tuned between low-viscosity spherical micellar solutions and highly elastic solid-like gels by addition of NaOH or HCl. Studies have shown that incorporating a pH-sensitive hydrotrope into surfactant solutions is also a viable approach for tuning [11–13]. Zonglin and Yujun [8] added *N*-erucamidopropyl-*N*,*N*-dimethylamine into maleic acid solutions and found that the viscosity of micellar solution is switchable by tuning the pH through addition of a minor acid or base.

Most of the pH-responsive WLMs that have reported were created by using cationic surfactants [14]. By contrast, anionic systems have rarely been reported. Anionic surfactants are more biodegradable and less toxic than cationic surfactants [15,16]. Therefore, devoting effort to develop novel pH-responsive WLMs based on anionic surfactants is necessary. Sodium oleate (NaOA) is an environment friendly anionic surfactant that plays a key role in many industrial applications, including oil and cosmetic production. NaOA alone cannot form WLMs; salts, cationic surfactants, or other additives are often used to prepare WLMs [16,17]. However, the pH-responsiveness of NaOA-based WLMs is rarely reported.

Synthesis of mesoporous silicas (MSs) relies on surfactant (S) micelles, which serve as templates for the assembly and for the subsequent and/or simultaneous condensation of inorganic precursors (I) [18,19]. The isoelectric point (PI) of silicas is approximately 2.0, and silicas are positively charged (I^+) at pH < 2 and negatively charged (I^-) at pH > 2 because of protonation of silica species [20]. MSs exhibiting different mesoporous structure have been synthesized successfully. Based on the type of interaction, different synthesis routes are classified as follows: S^+I^-, $S^+X^-I^+$, S^0I^0, $(S^0H^+)(X^-I^+)$, S^-I^+, and $S^-X^+I^-$, where X represent a counter ion, and their charge varies depending on whether they are in a cationic, anionic, or neutral form. Therefore, the choice of surfactants and reaction conditions determines the interactions that drive formation of mesostructured silica. Although various surfactants are commercially available, only a few can be used as templates to synthesize mesoporous materials [21]. Therefore, investigating the new surfactant templates is necessary.

This paper reports anionic wormlike micellar (WLM) system formed by sodium oleate (NaOA) and benzyltrimethyl ammonium bromide (BTAB). By changing the pH of the NaOA–BTAB mixed micelles, we can regulate the transformation between NaOA and oleic acid. The pH-induced changes in the microstructures of the assemblages were investigated through rheological measurements and dynamic light scattering (DLS) measurements. The anionic WLMs were then used as templates to synthesize MSs, and we attempted to explain the possible mechanism of MS formation. This approach not only provides a new idea for researchers to synthesize mesoporous materials but also expands the potential applications of anionic WLMs.

2. Materials and methods

2.1. Materials

NaOA (>97%) was produced by TCI. BTAB and tetraethyl orthosilicate (TEOS) were supplied by Aladdin Industrial Corporation (China). Sodium hydroxide and absolute ethyl alcohol were produced by Guangzhou Chemical Regent Factory (China). Deionized water was through the experiment.

2.2. Sample preparation

NaOA and BTAB solutions were prepared using ultrapure water. The concentration of NaOA and BTAB in the solutions used in our experiment was 0.12 and 0.2 mol L^{-1}, respectively. All of the samples we used were thoroughly mixed through magnetic agitation, and the pH values of the samples were adjusted by adding NaOH or HCl. The samples were mixed at 50 °C in a thermostat-controlled water bath. TEOS was subsequently added into the above mixture, which was placed in a thermostat-controlled condition at 50 °C for 24 h. The molar composition of the mixture was 0.6 NaOA:1 BTAB:0.045 TEOS:277.8 H_2O. The mixture was filtrated, centrifuged, and washed thoroughly with ethanol and water. The product was dried and then calcined at 600 °C for 6 h to remove the surfactant template.

2.3. Rheological measurements

The rheological properties of all the samples was measured by a stress controlled rheometer (Discovery DHR, TA Instrument) by using 60 mm plate geometry, and the plate temperature was controlled by a Peltier unit. Frequency spectra was conducted in the linear viscoelastic regime of the samples determined from dynamic strain sweep measurements