



A facile route to design pH-responsive viscoelastic wormlike micelles: Smart use of hydrotropes

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ABSTRACT

A simple and effective route to design pH-responsive viscoelastic wormlike micelles based on commercial compounds is reported. According to this route, pH-sensitive viscoelastic fluids can be easily obtained by introducing a pH-responsive hydrotrope into a surfactant solution. In this paper, the mixed system of cetyltrimethylammonium bromide (CTAB) and potassium phthalic acid (PPA) was studied in detail. This pH-sensitive fluid can be switched between a gellike state and a waterlike state within a narrow pH change. Rheology and DLS results revealed that the pH-sensitive flowing behavior was attributed to the microstructure transition between wormlike micelles and short cylindrical micelles. Combined with fluorescence anisotropy, NMR, and UV-vis, it was demonstrated that the pH response of viscoelastic fluid originated from the different binding abilities of hydrotrope to surfactant as pH varies. Furthermore, different kinds of hydrotropes can be utilized to prepare pH-responsive viscoelastic fluids in the desired pH areas.

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1. Introduction

Molecular self-assembly of surfactants based on noncovalent interactions provides a powerful tool for the creation of well-defined structures in the nanometer or micrometer length scale, such as sphere, rod, fiber, disc, and tube [1–5]. Under certain conditions, global micelles may undergo enormous elongation and form very long and highly flexible aggregates, referred to as “wormlike” or “threadlike” micelles. Above a critical concentration c^* , wormlike micelles may entangle into a transient network, which display remarkable viscoelastic properties [6–10]. Viscoelastic wormlike micelles formed by low molecular weight compounds have drawn considerable interest over the past two decades due to their superior properties and wide applications as heat-transfer fluids, drag reduction agents, hard-surface cleaners, fracturing fluids in oil fields, personal care products, and templates for nanomaterial synthesis [11–14]. In recent years, particular interest is focused on the design of viscoelastic fluids that are responsive to external stimuli, such as light [15–17], electric [18], ultrasound [19], pH [20,21], temperature [22–24], and metal ion [25,26]. These stimuli-responsive viscoelastic fluids (called “smart viscoelastic fluids”) can

find applications in clutches for transmission [27], shock absorbers [28], vibration control [29], and human muscle stimulators [30].

Compared to other external stimuli, pH is a simple and applicable tool for controlling viscoelastic fluids. However, up to now only a few works have been reported concerning pH-responsive viscoelastic fluids based on small organic molecules. Maeda and co-workers have demonstrated that ionization of tetradecyldimethylamine oxide has marked effects on the viscoelastic properties of the micelle solutions. Later, reversible conversion of wormlike micelles to vesicles of oleyldimethylamine oxides with increase of ionization degree was observed by the same group [20,21]. Apart from wormlike micelle solution, hydrogel formed by three-dimensional networks is another kind of viscoelastic fluid that has attracted great attention [31]. Stupp and co-workers have obtained pH-responsive hydrogels constructed by nanofibers with 12 derivatives of peptide-amphiphile molecules [32]. Xu, Li, and co-workers created a reversible sol–gel transition modulated by pH from a multipyridyl-based supergelator [33]. In addition, Hamachi and co-workers reported a pH-responsive supramolecular hydrogel composed of two small amphiphilic molecules [34]. These studies offer the advantage of controllable pH-responsive viscoelastic fluids through a similar strategy, that is, incorporating pH-responsive moieties into amphiphiles covalently through organic synthesis.

However, more effort should be made to overcome the disadvantages of this strategy before these responsive viscoelastic fluids

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can be applied to industrial areas. First, this strategy relies on novel synthetic amphiphiles with pH-responsive functional groups, which require a time-consuming and low-yield organic synthesis. The synthesis process of these novel amphiphiles may greatly restrict further application of these responsive viscoelastic fluids. Second, a given pH-responsive viscoelastic fluid can only be modulated within a suitable pH area, named as pH_{eff} . In principle, the pH_{eff} was mainly determined by the pH-responsive group attached to the amphiphile. For the consideration of industrial applications, it is necessary to prepare different pH-responsive viscoelastic fluids with various pH_{eff} . Consequently, a series of organic syntheses should be conducted to incorporate different pH-responsive functioning groups to amphiphiles. Based on the above consideration, it is necessary to develop a simple and effective route for preparing pH-responsive viscoelastic fluids with various pH_{eff} without complicated organic synthesis.

In this paper, a new strategy for preparing pH-responsive viscoelastic fluids by incorporating pH-responsive moieties to amphiphiles noncovalently is suggested. The mixture of hydrotrope and conventional surfactant was selected since hydrotropes can strongly bind to the amphiphile head group noncovalently through electrostatic attraction and hydrophobic effects, which greatly promotes the elongation of wormlike micelles. In addition, various hydrotropes bearing different pH-responsive groups are commercially available, such as $-COOH$, $-NH_2$, $-ArOH$, $-OPO_3H_2$, and $-PO_3H_2$.

From this perspective, a pH-responsive viscoelastic fluid was designed with a conventional surfactant and hydrotrope, i.e., cetyltrimethylammonium bromide (CTAB) and potassium phthalic acid (PPA). This viscoelastic fluid can be switched between highly viscoelastic solution and waterlike solution within a narrow pH change, which was attributed to the transition between wormlike micelles and short cylindrical micelles. Such pH-responsive microstructure transition was rationalized from a perspective of molecular packing with the aid of NMR, UV-vis, and fluorescence anisotropy. Furthermore, a series of pH-responsive viscoelastic fluids with different pH_{eff} was obtained according to this strategy. Finally, the possibility of applying this strategy to design stimuli-responsive self-assembled organization is discussed.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide and cetylpyridinium bromide were products of A.R. Grade of Beijing Chemical Co. and recrystallized five times from acetone and ethanol before use. 1-Cetyl-3-methylimidazolium bromide was synthesized and purified according to Ref. [48]. Other compounds were of A.R. grade.

2.2. Rheological measurements

The rheological properties of samples were measured with a ThermoHaake RS300 rheometer. Cone and plate geometries were used in each case. The temperature was controlled at $25 \pm 0.05^\circ C$. A solvent trap was used to minimize water evaporation. Frequency spectra were conducted in the linear viscoelastic regime of the samples determined from dynamic strain sweep measurements.

2.3. DLS measurements

DLS was performed with a spectrometer (ALV-5000/E/WIN Multiple Tau Digital Correlator) and a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength). The scattering angle was 90° , and the intensity autocorrelation functions were analyzed by using the methods of Contin.

2.4. NMR measurements

1H NMR was carried out in solutions of D_2O with Mercury Plus 300 MHz. The NMR measurement was carried out at $25^\circ C$.

2.5. UV-vis measurements

UV-vis spectra were carried out on a spectrophotometer (Cary 1E, Varian Australia PTY Ltd.) equipped with a thermostated cell holder. The UV-vis measurements were all carried out at $25^\circ C$.

2.6. Fluorescence anisotropy

Steady-state fluorescence anisotropy (r) was measured on a F4500 Hitachi spectrofluorometer equipped with a thermostated cell holder and filter polarizers that used the L-format configuration [35]. 1,6-Diphenyl-1,3,5-hexatriene (DPH) was used as the fluorescence probe. The concentration of DPH was adjusted to 1.0 μmol by adding an appropriate amount of 1.0 mmol ethanol stock solution of the probe. The excitation wavelength was 350 nm and the emission was monitored at 430 nm. The r value was calculated employing the equation

$$r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH}), \quad (1)$$

where I_{VV} and I_{VH} are the fluorescence intensities polarized parallel and perpendicular to the excitation light, and G is the instrumental correction factor ($G = I_{VV}/I_{VH}$).

3. Results and discussion

3.1. pH-sensitive rheological properties and microstructure transition

Fig. 1a shows the appearance of viscoelastic fluid containing mixtures of 60 mM CTAB and 40 mM PPA. At pH 3.90, the sample is transparent and viscous enough to support its own weight. As pH was adjusted to 5.35, the sample shows a waterlike flowing behavior.

Steady and dynamic rheological measurements were performed to investigate the flowing properties as pH value varies. At pH 3.9, the system shows a shear thinning flowing behavior with a viscosity plateau of 75,000 cP (Fig. 1b). Dynamic rheological measurement (Fig. 1c) indicates a strong viscoelasticity of this solution. The elastic modulus G' and viscous modulus G'' exhibit a good fit to a single-relaxation-time Maxwell model, given by the equations below:

$$G'(\omega) = \frac{G_0(\omega t_R)^2}{1 + (\omega t_R)^2}, \quad (2)$$

$$G''(\omega) = \frac{G_0\omega t_R}{1 + (\omega t_R)^2}. \quad (3)$$

Here, G_0 is the plateau modulus, and t_R is the relaxation time estimated as $1/\omega_c$, where ω_c is the crossover frequency at which G' and G'' intersect. Also the "Cole-Cole" plot of G'' versus G' (see Fig. S1 in Supplementary material) reveals the semicircle characteristic of a Maxwell fluid, which is expressed as

$$G''^2 + \left(G' - \frac{G_0}{2}\right)^2 = \left(\frac{G_0}{2}\right)^2. \quad (4)$$

The steady shear and dynamic oscillation response strongly suggest the existence of wormlike micelles in the mixture of 60 mM CTAB and 40 mM PPA at pH 3.90.

As pH increases, the viscosity of the sample drops remarkably. When pH reaches 5.35, the sample exhibits a Newtonian flowing behavior with a low shear viscosity of 1.1 cP (Fig. 1b). Dynamic rheological measurement indicates a gradual decrease of elastic

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