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Wormlike micelles with pH-induced rheological property formed by cationic surfactant/anthranilic acid mixed aqueous solution

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ABSTRACT

The pH-induced rheological property of octadecy trimethyl ammonium bromide with anthranilic acid was investigated. The viscoelasticity property and structural transformation of molecular self-assembly were comprehensively discussed by means of rheological measurements, dynamic light scattering and cryogenic-transmission electron microscopy. On the basis of surface tension results, the change of viscoelasticity was explained by calculating the packing parameter of *P*. UV–vis results confirmed that the pH-dependent interaction between the aromatic ring of anthranilic acid and the head group result in the transition between WLMs and spherical micelles, thus altering the viscoelasticity of WLMs.

1. Introduction

Over the past decades, molecular self-assembly of surfactants has drawn widespread attentions both from fundamental theory scientists and industrial engineers due to its unique molecular structure [1–3]. Among various surfactants aggregates, including micelles, vesicles, lamellar, sponge, etc., threadlike micelles or wormlike micelles (WLMs) are always a great important field of current research on account of their superior rheological property and particular micellar structures [4,5]. Under appropriate temperature, concentration and salinity environmental conditions, global micelles may undergo enormous elongation and form long flexible WLMs. Because of the former also possess excellent viscoelasticity, entanglement of WLMs is similar to polymers in aqueous solution. However, the greatest difference between the two is the network of WLMs is capable of continuously breaks and recombines due to WLMs exist in a dynamic equilibrium [6]. And for exactly that reason, WLMs have good performance in many aspects such as home and personal care, drug delivery, oil industry, and drag reduction agents [7–10].

Recently, smart wormlike micelles have received close extensive attention and research, which because physicochemical properties can be controlled by environmental stimuli such as UV/vis light, pH, redox reaction and temperature [11]. Compared with the other stimuli, pH-stimuli has many advantages such as fast response, cheap, nontoxic, abundant and easy operating. Therefore, many scientists from all over the world have investigated the pH-induced WLMs in aqueous solutions over the past decades. From what has been reported in a large body of literature, two approaches were generally utilized to obtain pH-induced WLMs [12]. One is directly utilizing surfactants bearing pH-responsive functional groups. Feng's team developed a novel pH-switchable WLMs system consisted of natural erucic acid without the addition of hydrotropes [13]. Zhang and coworkers investigated a wormlike micelle solution of erucyldimethyl amidopyrine amine oxide (EMAO) [14]. EMAO show striking pH sensitivity at high temperature but exhibit inconspicuous pH sensitivity under room temperature. A more common route is formed by introducing hydrotropes featuring environmentally sensitive groups. Huang' group introduced the pH-sensitive potassium phthalic acid into cetyltrimethylammonium bromide (CTAB) solution [15]. This pH-sensitive system can be switched between "on" and "off" two states within a narrow pH response window. Therefore, we intend to test the feasibility of creating a pH-induced WLMs by introducing hydrotropes featuring environmentally sensitive groups.

In the present study, the pH-induced WLMs composed of octadecy trimethyl ammonium bromide and anthranilic acid was investigated. Cryogenic-transmission electron microscopy (Cryo-TEM), dynamic light scattering, surface tension measurement, UV–vis spectrum measurement and rheological measurements were used to investigate the self-assembly in aqueous solution. Furthermore, the variety of pH values effect on the structure of the self-assembly was studied.

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2. Materials and methods

2.1. Materials

Octadecy trimethyl ammonium bromide (OTAB) was synthesized as described previously [18]. Anthranilic acid (AA) was purchased from Aladdin Chemistry Company. Sodium hydroxide and hydrochloric acid was purchased from Sinopharm Chemical Reagent Company and was used without any purification.

2.2. Physicochemical analysis

A rotational rheometer equipped with a cylindrical rotor (HAAKE MARS III) was employed to perform rheological tests at 25 °C. Two different types of rheological measurements were carried out. One was steady shear rate viscosity measurements and the shearing rate was set to a range of 0.01–1000 s^{-1}; another one is oscillatory shear measurements and the frequency region ranged from 0.01 to 100 $rad\cdot s^{-1}$. DLS analyses were conducted by a laser particle size analyzer (Malvern) with solid-state He − Ne laser. The scattering angle was set at 90° and the incident beam wavelength was set at 632.8 nm. To ensure temperature homogeneity of the samples, each sample required equilibrating at 25 °C for 15 mins. Each sample was needed to test three times to ensure the reproducibility of DLS results. Cryo-TEM images were prepared at a 120KV JEM-1400 Plus TEM instrument. The samples were stored in a controlled environment vitrification system. First of all, approximately 5 mL of the sample was added onto a perforated polymer film. After 10 s, the polymer film was immediately immersed into a − 170 °C liquid ethane reservoir. Before the observation, the sample needs to be placed in the liquid nitrogen environment. UV–vis spectrum analysis was performed with a UV–vis 2601 spectrophotometer (Unico, USA) at 25 °C the wavelength range of spectrophotometer was maintained at 190–300 nm. The Du Noüy ring method was used to measure surface tension on an automatic surface tension instrument (Chengde dahua factory, JWY-200B, China) at 25 ± 0.1 °C. Before each experiment, the instrument was adjusted by measuring the surface tension of distilled water.

3. Results and discussion

3.1. pH-sensitive rheological properties of OTAB-AA system

As verified by early research, the micelle structure of OTAB in aqueous solution could be transformed between spherical micelles and WLMs under the influence of organic or non-organic counterion salts [19]. On the basis of the preceding point, it is anticipated that the OTAB-AA mixed solution can form WLMs aggregates. The steady shear measurements were first carried out under different pH value. Fig. 1 illustrates the steady shear viscocity-shear rate curve of 100 mM OTAB-AA mixed solutions. Due to the presence of spherical micelles, one can clearly find that the solution of initial pH value (2.52) displays the typical characteristic of a Newtonian fluid, which viscosity is independent of any shear rate. When adjusting the pH value to 3.06, the similar phenomenon is still present, merely the viscosity of the solution slightly increases. However, 100 mM OTAB and 100 mM AA mixed solution at pH 4.05–6.02 displays a Newtonian fluid evident behavior at low shear rate and then followed by a shear-thinning behavior when the shear rate exceeds a critical value. The typical shear-thinning behavior is generally regarded as the formation of WLMs [20]. At the low shear rate, WLMs show the nature of the Newtonian fluid that constant viscosity is independent of shear rate. At the high shear rate, the alignment of WLMs chains under direction flow induced by high-speed shearing causes the fall of viscosity. When pH is further increased to 7.08, Newtonian fluid behaviors reappear, reflecting the transition from spherical micelles to WLMs network then back to spherical micelles.

To better understand the influence of pH, the zero shear viscosity (η_0) is plotted against the pH values. From the results shown in Fig. 2, the η_0 of OTAB-AA first maintains basically unchanged when pH < 3.06; then drastically rises with a small pH change when pH > 3.06, followed by another viscosity plateau with a gel-like behavior in the range of 4.05–5.07; after that the η_0 quickly jumps down and finally reaches a plateau with another low viscosity region when pH > 6.02. From the variation of η_0 with the increase of pH described above, one can easily deduce that the aggregation formed in the OTAB-AA solutions undergoes a process of WLMs formation–disruption [21].

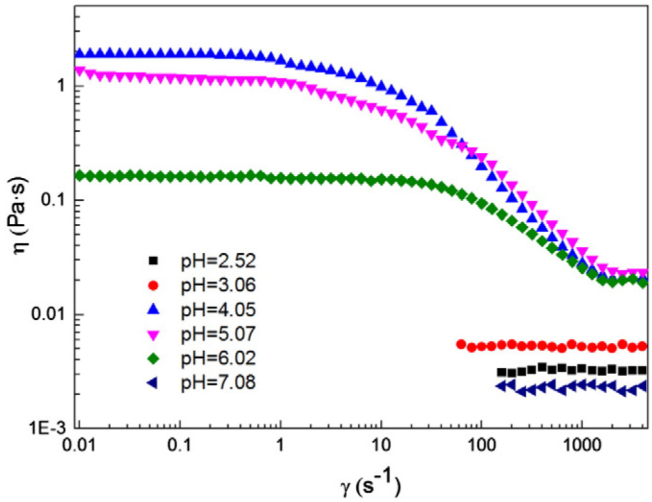

Fig. 1. Steady rheology plots for 100 mM OTAB-AA aqueous solutions with different pH values.

Oscillatory shear measurements were also carried out and Fig. 3 exhibits dynamic frequency spectra of the 100 mM OTAB-AA mixed solution at different pH values. The data are depicted as plots of the storage modulus (G') and loss modulus (G'') as functions of the oscillatory shear frequency (ω) at a fixed shear stress ($\sigma = 1$ Pa). As showed in Fig. 2a, G′ is lower than G″ at low shear frequency region initially. Finally, G′ crosses (critical shear frequency ω_c) and prevails over G''. That is to say, solutions appear an evident viscous behavior before ω_c and show a typical elastic response after ω_c. Therefore, the solution is viscoelastic, and its relaxation time τ_R (~$1/\omega_c$) is finite, which is normally accounted for the entanglement of WLMs [5].

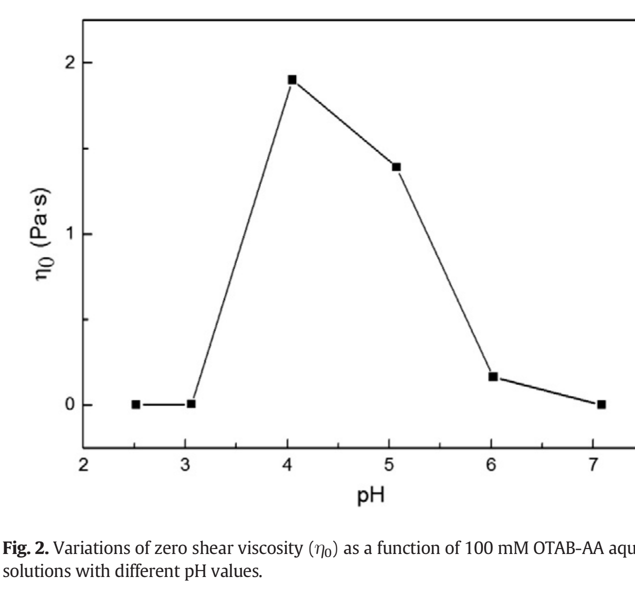

Fig. 2. Variations of zero shear viscosity (η_0) as a function of 100 mM OTAB-AA aqueous solutions with different pH values.