Rheological behavior and physico-chemical properties of cetyltrimethylammonium salicylate in aqueous solutions

Ali Ping, Panpan Du, Xilian Wei *, Dezhi Sun, Junhong Zhang, Jie Liu, Xinran Zhong

Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, PR China

ABSTRACT

Rheological experiments of cetyltrimethylammonium salicylate (C_{16}TASal) solution were carried out on the micellar solutions as a function of surfactant concentration and temperature. This system forms short, rod-like micelles at concentrations of 1–15% as determined by transmission electron microscopy. Rheological behavior at low concentration displays gel-like behavior up to 3%, while it follows Maxwell fluid behavior with a single stress relaxation time above 3%. By the single crystal diffraction experiment, it can be found that the gel-like and Maxwell-like viscoelasticities originate in a three-dimensional network formed by hydrogen bond linkages between short rod-like micelles, connecting carboxyl groups of salicylate anions and water molecules. The high viscosity is from the linkages between short rod-like micelles rather than from entangled long micelles.

The electronic conductivities of C_{16}TASal solution of dilute solution and semi-dilute solution have been studied. The conductivity–concentration curves of dilute solution show two breaks which correspond to two characteristic concentrations of C_{16}TASal solution. The first break point corresponds to the critical micelle concentration (cmc). The second break point corresponds to the transition concentration (C_t), where the system begins to form rod-like micelles. The conductivity of semi-dilute solution slightly decreases with the increasing temperature.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The physical properties, phase behavior, and rheology of aqueous solutions of cationic surfactants are very sensitive to changes of counterions [1–5]. There are many more studies of the effect of counterions on the self-assembly of cationic surfactants in aqueous solution than of anionic surfactants. Cetyltrimethylammonium chloride (CTAC) micelles remain nearly spherical over a large range of concentration from 0.16 to 1.2 mol L^{-1}, even in the presence of NaCl [6,7]. On the other hand, the cetyltrimethylammonium bromide (CTAB) micelles are prolate at their cmc (0.92 mmol L^{-1}), become rodlike with increasing surfactant concentration, and begin to entangle at concentration above 40 mmol L^{-1} [8]. The behavior of micellar CTAB solutions can be described by the theoretical treatments presented for solutions of entangled polymer chains in semi-dilute range. In salt-free aqueous C_{16}TASal solutions, rodlike micelles of C_{16}TASal form at concentrations just above the critical micelle concentrations (0.15 mmol L^{-1}), as demonstrated by 'H

NMR self-diffusion measurements by Olsson et al. [9]. These differences in behavior arise from differences in counterion binding to micelles. Here, the degree of counterion binding to cationic micelles increases in the order Cl$^-$ < Br$^-$ < salicylate.

For the aqueous C_{16}TASal solution considerable theoretical and experimental work has been done due to these special characteristics [3,9–15]. Aqueous C_{16}TASal solutions display spinnability and viscoelasticity even at dilute concentrations. Light-scattering shows that short rodlike micelles are formed in aqueous solutions and produce pseudo-linkages through salicylate ions [10], so inter-micellar correlation is quite apparent.

In this work, we explore in detail microstructures and rheological characteristics of semi-dilute micellar solutions of C_{16}TASal. The effects of surfactant concentration (from 1 to 15 mass%) and temperature (from 15 °C to 35 °C) on the structure of wormlike micelles are investigated by employing viscosity measurements and transmission electron microscopy and discussed from the crystal structure and the hydrogen bonds formed between salicylate counterions. We also investigate the critical micelle concentration (cmc) and the transition concentration from globular to rodlike micelles, C_t, have also been determined from 25 °C to 50 °C by electrical conductivity measurements.

* Corresponding author. Tel.: +86 635 8230613; fax: +86 635 8239196.
E-mail addresses: weixilian@lcu.edu.cn, weixilian123@126.com (X. Wei).

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium salicylate (C_{16}TASal) was synthesized in our laboratory. Cetyltrimethylammonium chloride (CTAC) and sodium salicylate (NaSal) at the molar ratio 1:1 were dissolved in mixed solvents of ethanol with acetone at ratio 1:3 in volume. The mixed solution was then heated at 50 °C, the insoluble NaCl was then filtered off. The C_{16}TASal was purified by recrystallization from ethyl acetate, and the purity of the final product was determined by the Mohr precipitation method (the recrystallization was considered complete when no AgCl precipitate was detected when the filtrate was added to a $AgNO_3$ solution) and the sodium analysis was performed by using an inductive coupled plasma-atomic emission spectroscopy (ICP-AES), and there is no characteristic emission line of Na^+. CTAC and NaSal (Aldrich Chemical Reage Co.) were the special grade reagents used as received. The water used in solution preparation was redistilled from alkaline potassium permanganate, which insures that the surface tension of water is 72.7 mN m^{-1} at 20 °C, and the electrical conductivity of water is 1.10 μs cm^{-1} at 20 °C.

2.2. Methods

2.2.1. Rheological measurements

Samples were prepared at the given weight percentage of the surfactant and were homogenized by a vortex mixer at 50 °C until homogenization then they were left in water bath at desired temperatures, for at least 1 week to ensure equilibration before performing measurements. All the samples were centrifuged to remove suspended air bubbles before being tested. Rheological measurements were performed on a stress controlled rheometer (AR2000ex, TA Instruments, USA) with cone-plate geometry. The cone is made of standard ETC steel with a cone diameter of 20 mm and cone angle of 2°. The gap between the center of the cone and plate is 50 μm. The measuring unit was equipped with a temperature unit (Peltier plate) providing a rapid change of the temperature and an accurate temperature control (±0.05 °C) over an extended time for all the temperatures considered in this work. To prevent errors due to drying on the sample surface, the measuring device is surrounded by a solvent trap containing water. Frequency sweep measurements were performed at a given stress σ₀ (chosen in the linear domain where the amplitude of the deformations is very low) in the frequency (ω) region varying from 0.001 rad s^{-1} to 1000 rad s^{-1}. Each measurement was repeated three times to ensured good reproducibility (better than 1%).

2.2.2. Electrical conductivity measurement

Conductivity of the surfactant solutions was measured as a function of concentration with a low-frequency conductivity analyzer (Model DDS-308, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy of ±1%) at six different temperatures, and the measurements were repeated twice at each temperature.

2.2.3. Single-crystal X-ray diffraction

Well-shaped crystals got from the surfactant solution were sealed in Lindemann capillaries under nitrogen. All of the diffraction data were collected at 25 °C on a Bruker SMART 1000 diffractometer. The structures were solved by direct methods. Their contributions to structure factor calculations were included. Crystallographic parameters and refinement details are listed in Table 1 of Supplementary Information.

2.2.4. Electronic microscopy

Samples for electron microscopy were prepared by freeze-fracture replication according to standard techniques. Fracturing and replication were carried out in a high-vacuum freeze-etching system (Balzers BAF-400D). Replicas were examined in a JEM-2100 electron microscope (JEOL Co., Japan).

3. Results and discussion

3.1. Effect of surfactant concentration

3.1.1. Viscoelastic properties of C_{16}TASal solutions at different concentration

Transparent, gel-like solutions were formed in the concentration range of 1–15% (Fig. 1a).

Oscillatory shear rheology of viscoelastic micellar systems at low shear frequency generally follows Maxwell fluid behavior with a single stress relaxation time, τ_R. The relaxation time, τ_R, is estimated from ω_c^{-1}, where ω_c is the frequency at which two modules are equal. The storage modulus, G', the loss modulus, G'', and the complex viscosity, $G'_\infty = 2G''_{max}$ of the systems are given by Eqs. (1)–(4) [16].

$$G' = \frac{(\omega\tau_R)^2 G'_\infty}{1 + (\omega\tau_R)^2} \tag{1}$$

$$G'' = \frac{\omega\tau_R G'_\infty}{1 + (\omega\tau_R)^2} \tag{2}$$

$$|\eta^*(\omega)| = \frac{(G'^2 + G''^2)^{1/2}}{\omega} \tag{3}$$

At high ω, the storage modulus G' attains a limiting value called a plateau modulus, G'_∞. Also, for the systems showing deviation from Maxwell behavior, the value of G'_∞ may be estimated from the modulus value of ω_c by using the relation $G'_\infty = 2G''_{max}$, where G''_{max} is the viscosity modulus at shear frequency ω_c, and $|\eta^*(\omega)|$ is the zero-shear-rate viscosity. Also the interesting is that the Cole–Cole plot of storage modulus G' versus loss modulus G'' reveals the semicircle characteristic of a Maxwell fluid, which is expressed as

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

Fig. 1b–d shows the dynamic rheological spectra of C_{16}TASal solution at different concentrations (1–15 mass%). No Cross-over points are detected for the samples below 5%, but have the plateau in G' curves and G' wholly exceeds G'' throughout the examined frequencies, which are in accord with the gel-like behavior [2,17]. For the systems of concentrations over 5%, elastic or storage modulus (G') is always smaller than viscous or loss modulus (G'') at low frequencies. As frequency increases, both G' and G'' increase and cross at a frequency ω_c, which corresponds to the relaxation time being fit by a simple Maxwell model. G'' appears a maximum in ω_c, then decrease, and then passes through a minimum with increasing frequency. After this minimum, G'' increases again indicating at least a second relaxation time at a frequency beyond the limit of the rheometer (100 rad s^{-1}) [18], but there is not enough high-frequency data to accurately determine G'_∞ and τ_R of the second maximum in the process of our measurements. The deviation of G'' from the model at the high ω region is another characteristic of wormlike micelles [19], which corresponds to the fact that wormlike micelles are in a dynamic equilibrium and there are rapid breaking and recombination processes [20].

Fig. 2a represents good fitting results for two typical cases of the system in the ranges of low and medium frequencies (solid lines). It is sometimes difficult to determine how "good" a Maxwell model