ORIGINAL ARTICLE

In-Situ Formation of Viscoelastic Wormlike Micelles in Mixtures of Non-Surface-Active Compounds

Yongmin Zhang · Dapeng Zhou · Yujun Feng

Received: 8 November 2013/Accepted: 18 March 2014/Published online: 3 April 2014 © AOCS 2014

Abstract Viscoelastic fluids based on surfactant selfassembled wormlike micelles have been in focus over the past decade. In this work, we report wormlike micellar solutions formed in situ by simply mixing two non-surfaceactive compounds, N-(3-(dimethylamino)propyl)palmitamide (C16AMPM) and salicylic acid (HSal), without specialized organic synthesis of a surfactant. In the absence of HSal, C16AMPM is poorly soluble in pure water; after introducing HSal, C16AMPM is protonated into quaternary ammonium, behaving like a cationic surfactant with a low critical micellar concentration (0.25 mM) and a small area per molecule, which favors the formation of long cylindrical wormlike micelles. Above the overlapping concentration (~ 28 mM), the wormlike micelles formed entangle each other into viscoelastic networks, enhancing the viscosity by several orders of magnitude. In contrast to the worms formed by a single ultra-long-chain surfactant, the current system shows the advantages of a smaller flow activation energy and end-cap energy, simpler formulation and lower cost, which make it more suitable for practical use.

Y. Zhang (🖂)

D. Zhou

Zhejiang Zanyu Technology Co., Ltd., Hangzhou 310030, People's Republic of China

Y. Feng (🖂)

Keywords Wormlike micelles · Viscoelastic fluids · Rheology · Surfactant · Salicylic acid

Introduction

Surfactant self-assemblies are of particular interest in numerous industrial processes. Above a critical micellar concentration (CMC), surfactant molecules generally form small globular micellar aggregates in aqueous solution, and may continuously grow uniaxially into very long and highly flexible wormlike micelles under some favorable physico-chemical conditions [1-3]. Typically, these threadlike micelles have a diameter of 2-5 nm and contour length ranging from several nanometers up to several micrometers [4, 5]. Above a threshold overlap concentration (C^*) , these linear micelles entangle into a dynamic transient network, displaying macroscopically remarkable viscoelastic properties reminiscent of polymer solutions. However, much unlike polymer chains connected by covalent bonds between monomers, wormlike micelles are held together by weak non-covalent hydrophobic interaction, constantly breaking and recombining, thus are also called as "living" or "equilibrium" polymers [6].

Over the past decades, considerable attention from both a theoretical viewpoint and industrial applications has been focused on wormlike micelles, due mainly to their unique aggregate microstructures and rheological responses [7]. From a fundamental perspective, wormlike micelles are particularly intriguing since they are models of "living polymers" [2, 8] for complex polymer systems. On the practical side, these viscoelastic fluids are good candidates for applications in the oil industry [9–12] including oilwell drilling, sand control, cleaning fracturing, self-diverting acidizing, and tertiary oil recovery, and show great

Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Materials Engineering, Jiangnan University, Wuxi 214122, People's Republic of China e-mail: zhangym@jiangnan.edu.cn

Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China e-mail: yjfeng@scu.edu.cn

potentials in biomedicine [13, 14], drag reduction [15, 16], home and personal care [17], to name but a few. So far, wormlike micellar solutions have been formulated with a wide variety of surfactants such as cationic [18–20], anionic [21, 22], zwitterionic [23, 24], and nonionic [25] species, as well as mixed formulations such as cationic– anionic [26], ionic–nonionic [27], ionic–zwitterionic [28], and nonionic–zwitterionic [29] systems. To the best of our knowledge, all the viscoelastic fluids mentioned above were formulated utilizing synthetic surfactant self-assemblies, few efforts have been put into the production of viscoelastic wormlike micelles through directly mixing two or more compounds of originally non-surface active agents.

Among the most popular wormlike micelles reported so far, those formed from the common cationic surfactant cetyltrimethyl ammonium bromide (CTAB) and a hydrotrope which is the most popular way. According to Hofmeister sequence [30], with increasing the binding capacity of counterions, the persistence length (l_p) of micelles decreases, and then the micellar flexibility increases. In other words, the counterions with strong binding capacity favor the formation of wormlike micelles. In contrast to non-organic counterions, organic ones are generally better at inducing the growth of micelles because they not only screen the electrostatic repulsion between charged hydrophilic headgroups of ionic surfactants, but also plug into the aggregates of surfactants owing to their strong binding ability. From what has been reported to date, it is confirmed that aryl-organic salts more readily induce the self-assembly of CTAB into elongated rod-like micelles than other hydrotropes [18–20]. However, few attempts have been made to fabricate viscoelastic fluids in situ utilizing non-surface-active aryl acid and a long-chain amphiphilic molecule.

Thus, here we have developed a wormlike micellar system by simply mixing two non-surface-active precursors: salicylic acid (HSal) and *N*-(3-(dimethylamino)propyl)palmitamide (C16AMPM) originated from natural palmitic acid, and examined the solubility, surface activities, as well as macroscopic rheological properties of a binary mixture in pure water.

Experimental Section

Materials

Palmitic acid (Chengdu Kelong Chemical Reagent Factory), *N*,*N*-dimethyl-1,3-propanediamine (DMPDA) (Rhodia Feixiang Specialty Chemicals), salicylic acid (HSal, Sinopharm Chemical Reagent Co., Ltd.) were used without further purification. All other chemicals used were of reagent grade, and were used as received. Triply distilled water by a quartz water purification system was used in all the measurements. Synthesis of *N*-(3-(Dimethylamino)Propyl)Palmitamide (C16AMPM)

50 mmol (12.82 g) palmitic acid, 75 mmol (7.66 g) DMPDA and 0.15 g NaF were put into a three-necked flask. The reaction mixture was refluxed 10 h at 155–160 °C under a N₂ atmosphere, during which the by-product H₂O was absorbed continuously by Al₂O₃. The excess of DMPDA was removed and the residue was washed with cold acetone (150 ml \times 2) (each time 10 ml water was added to remove NaF), followed by drying under a vacuum at -45 °C to obtain 15.8 g C16AMPM (yield 93 %) with a purity of 99.90 % (HPLC).

¹H NMR (300 MHz, CD₃OD), δ /ppm: 0.89 (t, J = 6.18 Hz, 3H), 1.26 (m, 24H), 1.60 (s, 2H), 1.71 (m, 2H), 2.16 (m, 2H), 2.20 (s, 6H), 2.40 (t, J = 7.68 Hz, 2H), 3.18 (t, J = 6.81 Hz, 2H).

Characterizations

¹H-NMR spectra of the C16AMPM, HSal and C16AMPM– HSal were recorded on a Bruker Avance 300 spectrometer at 300 MHz in CD₃OD at room temperature. Chemical shifts are expressed in ppm downfield from TMS as an internal standard. HPLC analysis was performed on a Waters HPLC system equipped with All-tech 2000 ELSD detector using a reverse phase (C18) column.

Preparation of Solutions

Different concentrations of mixture solutions were obtained by dissolving a specific amount of C16AMPM and HSal in triply distilled water with gentle agitation at 25 °C, and then the sample solutions were left for at least 24 h to reach equilibrium prior to measurements. The molar ratios of all the solutions were fixed at 1:1 unless otherwise stated, and the concentration of the solutions is given as the concentration of C16AMPM.

Surface Tension Measurement

Surface tension (γ) of the sample solutions was measured with a Krüss K100 tensiometer by the automatic Du Noüy ring model at 25 ± 0.1 °C, and a cover was used to minimize water evaporation. A set of measurements to obtain a stable surface tension was repeated until the change was <0.03 mN m⁻¹ every 3 min.

Rheology Measurement

Rheological properties of mixture solutions were determined on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with a concentric cylinder geometry CC27 (ISO3219), with a measuring bob radius of 13.33 mm and a measuring cup radius of 14.46 mm. Samples were equilibrated at the experimental temperature for not <20 min prior to the experiments. Dynamic frequency spectra were conducted in the linear viscoelastic region, as determined from prior dynamic stress sweep measurements. All measurements were carried out in the stress-controlled mode, and CANNON standard oil was used to calibrate the instrument before measurements. The temperature was controlled by a Peltier device, and a solvent trap was used to minimize water evaporation during the measurements.

Results and Discussion

Phase Behavior

There is no doubt that solubility or homogeneity of the mixture solutions is the primary consideration for further examination. Under a neutral or alkaline state, C16AMPM is hardly soluble in water due to its long hydrophobic tail and non-ionic headgroup, and behaves as a waxy solid at low temperatures or an oily paste at high temperatures, floating on the water surface. Nevertheless, the terminal tertiary amine groups in C16AMPM molecules can be protonated into quaternary species by the H⁺ ionized from HSal (p $K_a = 2.98$) [31] in aqueous solution, which improves the solubility of C16AMPM.

As shown in Fig. 1a, the quantity of HSal is initially too excessive to be completely dissolved, thus one can observe that the aqueous phase of the binary mixture solution and the solid phase (HSal crystal) coexist in the system. For example, when at $C_{C16AMPM}/C_{HSal} = 0.1:1$, the pH of the mixture suspension is 2.70. In this case, the solubility of HSal in water at 25 °C is about 15 mM [31], which is sufficient to protonate 10 mM C16AMPM molecules. Upon increasing C16AMPM content, the residual HSal content decreases and thus the pH value of the solutions increases slightly (Fig. 1b), indicating more and more that HSal molecules have been consumed through the protonation of C16AMPM. When the molar ratio of $C_{C16AMPM}$ / $C_{\rm HSal}$ goes up to 0.75:1, the HSal solid almost disappears from the bottom of the test tube, and the pH value starts rising rapidly (Fig. 1b). The solutions become homogenous when the molar ratio ranges from 0.75:1 to 1.5:1. If the C16AMPM concentration is further increased, phase separation occurs because of excessive C16AMPM. Hence, the molar ratio of $C_{C16AMPM}/C_{HSal}$ for the following experiments was fixed at 1:1 to ensure homogeneity of the solutions for further measurements.

¹H-NMR Confirmation of C16AMPM Protonation by HSal

To verify the protonation of C16AMPM in the presence of HSal, comparative ¹H-NMR studies were carried out on C16AMPM, HSal and the mixture of C16AMPM–HSal in CD₃OD, respectively. As exhibited in Fig. 2, for the mixture "C16AMPM–NaSal", the chemical shifts of the protons around tertiary amine group show an obvious downfield shift compared with C16AMPM alone, from 1.68 (peak "f"), 2.24 (g) and 2.38 ppm (h) to 1.90 (f_1), 2.86 (g_1) and 3.09 ppm (h_1), respectively, implying the protonation of tertiary amine group along C16AMPM [32, 33]. Whereas, the chemical shifts of the protons of Sal⁻¹ remain



Fig. 1 a Snapshots of and b pH variation of binary mixture solutions with varied molar ratios of $C_{C16AMPM}/C_{HSal}$, where C_{HSal} was fixed at 100 mM

Fig. 2 Comparison of the 1 H-NMR spectra for C16AMPM, HSal and C16AMPM–HSal using CD₃OD as the solvent





Fig. 3 The variation of surface tension with concentration at 25 °C

unvaried by contrast with HSal alone. In other words, the addition of HSal leads to the ionization of C16AMPM, transforming it into a cationic surfactant with anionic Sal^{-1} as the counterion.

Surface Activity

The surface activities of C16AMPM–HSal, HSal and C16AMPM were measured for comparison to further confirm the conversion of non-surface-active C16AMPM into a surfactant. Figure 3 shows the variation in surface

tensions of C16AMPM–HSal, HSal and C16AMPM against their concentrations in pure water at 25 °C, respectively. For C16AMPM or HSal alone, the surface tension nearly maintains constant with increasing concentration, and the value is comparable to that of pure water, suggesting that C16AMPM or HSal alone are non-surface-active. On the contrary, the surface tension of C16AMPM–HSal exhibits an evident drop with increasing concentration, and then reaches a plateau of 34.86 mN m⁻¹. The break point between the slope and plateau, generally taken as the CMC, is 0.25 mM, which is less than 1/3 that of CTAB (0.92 mM) [34]. This suggests that C16AMPM–HSal is surface active, which can dramatically decrease the surface tension of water with a small dose of C16AMPM–HSal.

The amount of adsorbed surfactant (Γ) at the air-water interface can be calculated using the Gibbs adsorption isotherm $\Gamma = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C}\right)$, and the area occupied (A) by a surfactant molecule at the air-solution interface can be obtained from the saturated adsorption $A = \frac{1}{N \cdot \Gamma_{CMC}}$ [35], where *R* is the gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the absolute temperature (K), *C* is the surfactant concentration (mol L⁻¹), $\partial \gamma / \partial \ln C$ refers to the slope below the CMC in the surface tension plot, *N* is Avogadro's number, and Γ_{CMC} is the maximum surface excess concentration at CMC. The value of *n* that stands for the number of species at the interface was taken as 2 for cationic surfactants [35]. Thus, the obtained value of Γ_{CMC} is 1.25 × 10⁻³ mM, about half of that reported for CTAB [34], while the *A* is 1.33 nm², which is 3 times larger than that reported for





CTAB [34]. This difference could be accounted for by the much larger counterion Sal⁻¹ for C16AMPM–HSal since their hydrophobic tail length is the same. Compared with Br^{-1} in CTAB, the Sal⁻¹ in C16AMPM–HSal has a bigger steric hindrance, concomitantly resulting in a looser adsorption layer at the air–water interface, i.e., a smaller Γ_{CMC} and a bigger A should obtain in this case.

Concentration Dependence on Rheological Behavior

The shape and size of the micelles rely not only on the geometry of the surfactant, but also on its surfactant concentration. Shown in Fig. 4 are the steady rheograms of C16AMPM-HSal solutions with different concentrations but at a fixed molar ratio of 1:1. As displayed in Fig. 4a, when the concentration of C16AMPM is <25 mM, the apparent viscosity of the mixture solutions is as small as that of water $(\sim 1 \text{ mPa} \cdot \text{s})$, and remains constant regardless of the shear rate, indicative of a typical Newtonian fluid. When C_{C16AMPM-HSal} is increased to 50 mM, the C16AMPM-HSal solution still behaves as a Newtonian fluid, but its apparent viscosity increases slightly, up to ~ 10 mPa·s, suggesting that the spherical micelles in the solution have evolved into short rodlike ones. Nevertheless, the dynamic network structures are not formed yet because the lengths of the rod-like micelles are still too short to entangle with each other. On further increasing the concentration to 75 mM, the C16AMPM-HSal solution displays a distinct rheological response, in which both Newtonian fluid behavior and the shear-thinning response are shown in low- and high-shear-rate regions, respectively, which are normally attributed to the formation of flexible wormlike micelles [3, 36]. In the initial low-shear-rate regime, the applied shear stress or strain is not big enough to impart any effect on the network entanglements, thus Newtonian behavior appears; whereas in the high-shear-rate region, the applied shear stress or strain is strong enough to cause the network entanglements to undergo a structural change when exceeding a critical shear rate at which shear-thinning starts to shift to lower values, rendering the alignment of long micelles along the flow direction, exhibiting shear-thinning behavior macroscopically.

When $C_{C16AMPM-HSal}$ is continuously increased, the viscosity of C16AMPM-HSal solutions is further enhanced due to the increasing network entanglement density and the critical shear rate decreases. However, when $C_{C16AMPM-HSal}$ goes up to 150 mM, the apparent viscosity continuously increases, but the variation is no longer as dramatic as that in the concentration range of 50–100 mM.

Zero-shear viscosity (η_0) of C16AMPM–HSal solutions, obtained by extrapolation of the shear viscosity along the Newtonian plateau to zero shear rate, is plotted as a function of $C_{C16AMPM-HSal}$ to check the dependence of $C_{C16AMPM-HSal}$ on viscosity. One can see in Fig. 4b that the η_0 –*C* curve is made up of two parts with a clear breakpoint, i.e., a critical overlapping concentration *C**. Below *C**, η_0 increases linearly in accordance with the Einstein equation [7, 29].

$$\eta_0 = \eta_{\text{water}} (1 + KC) \tag{1}$$

where *K* is on the order of unity; at this moment, the average micellar length usually increases with surfactant concentration following a simple power-law model with an exponent of ~1/2 [29]. Above C^* , η_0 increases exponentially by several orders of magnitude following the scaling law [7, 29].

$$\eta_0 \propto C^p \tag{2}$$

where p is the power-law exponent. This implicates that the wormlike micelles in the solutions start entangling with each other, forming a dynamic transient network, and then substantially imparting viscoelasticity to the solutions.

As shown in Fig. 4b, C^* of the C16AMPM–HSal system appears at around 28 mM, which is much higher than





those of the wormlike micellar solutions formed from longer chain surfactants, docosyl dimethyl carboxylbetaine (DDCB ~0.68 mM) [23] or sodium erucate (~8 mM) [21]. This moderate C^* of the C16AMPM–HSal worm solutions can be ascribed to its relative shorter hydrophobic tail to that of DDCB or sodium erucate. In the semi-dilute regime ($C > C^*$), the power-law exponent of η_0 against C16AMPM–HSal concentration is 6.2, slightly higher than the value predicted by the theoretical model for cationic worm solutions [37].

The shear frequency dependence of the storage and loss moduli (G' and G") on the concentration of the C16AMPM–HSal solutions is depicted in Fig. 5a. For all the solutions in the concentration range of 100–250 mM, G' crosses and prevails over G" when exceeding a critical shear frequency (ω_c). Namely, at low shear frequencies, the solutions show an evident viscous behavior, while a typical elastic response at high shear frequencies, implying that the C16AMPM–HSal solutions are viscoelastic and their relaxation times τ_R (~1/ ω_c) are finite. Furthermore, when $C_{C16AMPM–HSal}$ is increased from 100 to 250 mM, the plateau modulus G_0 (storage modulus at high frequencies) increases accompanied with decrease in ω_c , reflecting that the viscoelasticity at high concentrations is more pronounced than that at low concentrations.

The viscoelastic behavior of wormlike micellar solutions at low shear frequency often follows the Maxwell model with single relaxation time, which can be usually described by a semicircular shape of the Cole–Cole plots [29]:

$$G''^{2} + \left(G' - \frac{G_{0}}{2}\right)^{2} = \left(\frac{G_{0}}{2}\right)^{2}$$
(3)

in which the imaginary part G'' is plotted against the real part G'. As shown in Fig. 5b, for the Cole–Cole plots of C16AMPM–HSal solutions, G' and G'' have been normalized by the plateau modulus G_0 . At low frequencies, they fit the semicircle well over a majority of frequencies and deviations occurring at high frequencies owing to nonrepetitive effects [38, 39]. This suggests that the dynamic rheologic behavior of the C16AMPM–HSal solutions can be described by the single-mode Maxwell constitutive equation over a frequency range, indicative of the formation of wormlike micelles [37]. Moreover, the radius of the

semicircle and consequently the shear modulus increase steadily with concentration, which is generally attributed to the increase in G_0 and viscoelasticity [29].

To gain insight into the wormlike micelles formed by C16AMPM–HSal, the rheological parameters, G_0 and $\tau_{\rm R}$ (estimated via $1/\omega_{\rm c}$), were further investigated as a function of $C_{\rm C16AMPM-HSal}$. From the results shown in Fig. 5c, one can see that G_0 and $\tau_{\rm R}$ both rise steadily with increasing $C_{\rm C16AMPM-HSal}$, and both display power-law behavior as $G_0 \sim C^{\alpha}$ and $\tau_{\rm R} \sim C^{\beta}$ with $\alpha = 2.2$ and $\beta = 1.0$, respectively, very close to the theoretical forecast values 2.25 and 1.25 for entangled linear wormlike micelles [1, 6]; the power-law exponent of G_0 is also comparable to the value obtained for wormlike micelles of DDCB (2.1) [23].

According to Cates et al. [1] reptation or diffusion of wormlike micelles along their own contour network conforms to the stress relaxation mechanism. Thus the magnitude of G_0 is related to the density number of entanglement or mesh size in the network, and only depending on the surfactant concentration, whereas $\tau_{\rm R}$ is linked with the average length of the wormlike micelles, which is relevant to the concentration of both surfactant and hydrotrope. In the present system, only the surfactant concentration of C16AMPM-HSal varies. Hence, the increase in these rheological parameters with increasing $C_{C16AMPM-HSal}$ can be interpreted as the growth in the length of the wormlike micelles [40]. As C16AMPM-HSal concentration increases, the length and flexibility of the micelles rise concomitantly, and then the elongated micelles promote the increase of η_0 and τ_R . Furthermore, the growth of the micelles leads to an increase in the density number or mesh size of the aggregates, and thus the G_0 increases with increasing surfactant concentration.

Effect of Temperature on Rheological Behavior

As temperature also plays an important role in the practical applications of wormlike micellar solutions, it is necessary to investigate the influence of temperature on the micellar system formed by C16AMPM and HSal. Plotted in Fig. 6a is the temperature dependence of the steady rheological behavior of C16AMPM-HSal solutions with a fixed concentration of 150 mM. Within the temperature scope of 25-70 °C, the C16AMPM-HSal solution exhibits the coexistence of Newtonian fluid behavior at low shear rates and shear-thinning behavior at high shear rates, and the critical shear rate shifts to higher values and η_0 decreases monotonically with increasing temperature. Upon further increasing the temperature (80-90 °C), the shear-thinning behavior of the C16AMPM-HSal solution disappears in the shear rate range investigated here, and η_0 continues to decrease monotonically.

Additionally, a similar temperature effect is also observed for the oscillatory spectra of the C16AMPM– HSal solution (Fig. 6b). With increasing temperature, the critical shear frequency ω_c at which G' starts to cross and prevail over G" shifts to higher values. In other words, the relaxation time of the solution deceases with increasing temperature, and thus the reversible breaking–recombining process of wormlike micelles becomes faster. However, the plateau modulus G_0 remains nearly constant since it is independent of temperature, as is usually found in wormlike micellar solutions [39].

Generally, the key rheological parameters such as η_0 and τ_R of the C16AMPM–HSal solutions can be empirically described by the Arrhenius equation [1].

$$\eta_0 = G_0 A \mathrm{e}^{E_\mathrm{a}/RT} \tag{4}$$

$$\tau_{\rm R} = A e^{E_{\rm a}/RT} \tag{5}$$

where E_a is the flow activation energy in J mol⁻¹, and A is a pre-exponential factor. According to Eq. (4), G_0 is independent of temperature, which is also confirmed by the experimental results shown in Fig. 6b. However, the plots of η_0 and τ_R against 1,000/T both lie on straight lines with nearly the same slope (Fig. 7), indicative of Arrhenius behavior. Thus the E_a can be obtained from the temperature dependence of either η_0 or τ_R , and was found to 95 kJ mol⁻¹, which is comparable to that of wormlike micelles formed from CTAB–KBr (113 kJ mol⁻¹) [19], but is far less than those of wormlike micelles based on C22-tailed surfactants (160–198 kJ mol⁻¹) [22, 39].

According to Granek and Cates [38], if the entanglement length l_e is known, the micellar contour length \overline{L} can be estimated from rheological results through the following equation [38].

$$\frac{G_{\min}^{''}}{G_0} \approx \frac{l_e}{\bar{L}} \tag{6}$$

where G''_{\min} is the value of G'' at its minimum. As displayed in Fig. 6b, with increasing temperature, G''_{\min} also increases while G_0 maintains constant, signifying the increase in G''_{\min}/G_0 , or equivalently, the decrease of \overline{L}/l_e with temperature. Since G_0 is relatively independent of temperature, which is also confirmed by the experimental results (Fig. 6b), the mesh size and hence the entanglement length l_e are also independent of temperature [39]. Thus, as expected, the contour length \overline{L} decreases with increasing temperature, and the variation in \overline{L} with temperature can be quantified utilizing the mean-field theory [1].

$$\overline{L} \sim \varphi^{1/2} \mathrm{e}^{E_{\mathrm{c}}/2kT} \tag{7}$$

where φ is the volume fraction of surfactant, E_c is the endcap energy (J mol⁻¹) that is the energy required to create





a 10⁵

10⁴

Fig. 7 Zero-shear viscosity η_0 and relaxation time τ_R plotted as a function of the inverse of temperature for the 150 mM C16AMPM–HSal solution



two end caps by breaking a micelle, k is Boltzmann constant, 1.38×10^{-23} J K⁻¹.

Thus, E_c can be readily obtained from the slope of a semilogarithmic plot of $G_0/G''_{\min} \equiv \overline{L}/l_e$ vs 1/*T*, even without knowing the precise values of \overline{L} . From the results shown in Fig. 8, one can find that the plot of \overline{L}/l_e against 1,000/*T* falls on a straight line as well, thus the Arrhenius relationship for \overline{L} is confirmed, and the slope yields a value for E_c of 91 kJ mol⁻¹, which is more close to the E_c obtained for wormlike micelles formed from C16-tailed surfactants (ca. 50 kJ mol⁻¹) [19], but rather low compared to those reported for ultra-long-chain surfactant worms (160 kJ mol⁻¹) [39] or gemini surfactants systems (98–170 kJ mol⁻¹) [41].

The low E_c value denotes low energy cost for micellar scission; that is to say, the length of micelles is readily influenced by heating, leading to an exponential decrease

Fig. 8 The ratio of contour length \overline{L} and entanglement length l_e , plotted as a function of the inverse of temperature for the 150 mM C16AMPM–HSal solution

in rheological properties such as η_0 . Whereas within a low temperature range (25–40 °C), the wormlike micelles are presumably still long enough to entangle with each other so that the volume fraction of the giant entanglements remains constant, this is why G_0 remains constant throughout temperature increases.

Conclusions

Although it is well known that surfactants can selfassembly into wormlike micelles under appropriate conditions, displaying a viscoelastic response analogous to polymer solutions, most of the surfactants are obtained by organic synthesis prior to the experiments. Here, in contrast, we developed a wormlike micellar system simply by mixing C16AMPM and HSal. Before introducing HSal, C16AMPM is non-surface-active and poorly soluble in water. However, in the presence of HSal, C16AMPM is protonated into quaternary ammonium, behaving like a cationic surfactant with an anionic counterion Sal^{-1} . Due to a strong electrostatic screening capacity and binding ability of such a counterion, C16AMPM-HSal has a lower CMC and a smaller area per molecule than those of CTAB, and this favors the formation of long cylindrical wormlike micelles. With increasing concentration above C^* (~28 mM), the viscosity jumps by several orders of magnitude due to the formation of entangled wormlike micellar networks. Compared to ultra-long-chain surfactant worms, the current system shows some advantages such as lower E_a and E_c , simpler formulation and lower cost, which enable it to be an attractive candidate for some special applications particularly in oil and gas production.

Acknowledgments The financial support from the Fundamental Research Funds for the Central Universities (JUSRP11421) and the Natural Science Foundation of China (21173207) is gratefully acknowledged.

References

- Cates ME, Candau SJ (1990) Statics and dynamics of worm-like surfactant micelles. J Phys Condens Matter 2:6869–6892
- 2. Rehage H, Hoffmann H (1991) Viscoelastic surfactant solutions: model systems for rheological research. Mol Phys 74:933–973
- Dreiss CA (2007) Wormlike micelles: where do we stand? Recent developments, linear rheology and scattering techniques. Soft Matter 3:956–970
- Magid LJ (1998) The surfactant-polyelectrolyte analogy. J Phys Chem B 102:4064–4074
- Hoffmann H, Ebert G (1988) Surfactants, micelles and fascinating phenomena. Angew Chem Int Ed 27:902–912
- Cates ME (1988) Dynamics of living polymers and flexible surfactant micelles-scaling laws for dilution. J Phys Fr 49:1593–1600
- 7. Berret J-F (2006) In: Weiss RG, Terech P (eds) Molecular gels. Springer, Dordrecht
- Cates ME (1987) Reputation of living-polymers-dynamics of entangled polymers in the presence of reversible chain-scission reactions. Macromolecules 20:2289–2296
- Chase B, Chmilowski W, Marcinew R, Mitchell C, Dang Y, Krauss K, Nelson E, Lantz T, Parham C, Plummer J (1997) Clear fracturing fluids for increased well productivity. Oilfield Rev 9:20–33
- Al-Anzi E, Al-Mutawa M, Al-Habib N, Al-Mumen A, Nasr-El-Din H, Alvarado O, Brady M, Davies S, Fredd C, Fu D, Lungwitz B, Chang F, Huidobro E, Emmali M, Samuel M (2003) Positive reaction carbonate reservoir stimulation. Oilfield Rev 15:28–45
- Kefi S, Lee J, Pope TL, Sullivan P, Nelson E, Hernandez AN, Olsen T, Parlar M, Powers B, Roy A, Wilson A, Twynam A (2004) Expanding applications for viscoelastic surfactants. Oilfield Rev 16:10–23

- Li L, Nasr-El-Din HA (2010) Rheological properties of a new class of viscoelastic surfactant. SPE Prod Oper 25:355–366
- Afifi H, Karlsson G, Heenan RK, Dreiss CA (2011) Solubilization of oils or addition of monoglycerides drives the formation of wormlike micelles with an elliptical cross-section in cholesterolbased surfactants: a study by rheology, SANS, and cryo-TEM. Langmuir 27:7480–7492
- 14. Afifi H, Karlsson G, Heenan RK, Dreiss CA (2012) Structural transitions in cholesterol-based wormlike micelles induced by encapsulating alkyl ester oils with varying architecture. J Colloid Interface Sci 378:125–134
- Zakin JL, Zhang Y, Ge W (2007) In: Zana R, Kaler EW (eds) Giant micelles: properties and applications. CRC Press, Boca Raton
- Shi HF, Wang Y, Fang B, Talmon Y, Ge W, Raghavan SR, Zakin JL (2011) Light-responsive threadlike micelles as drag reducing fluids with enhanced heat-transfer capabilities. Langmuir 27: 5806–5813
- Yang J (2002) Viscoelastic wormlike micelles and their applications. Curr Opin Colloid Interface Sci 7:276–281
- Kern F, Zana R, Candau SJ (1991) Rheological properties of semidilute and concentrated aqueous solutions of cetyltrimethylammonium chloride in the presence of sodium salicylate and sodium chloride. Langmuir 7:1344–1351
- Candau SJ, Hirsch E, Zana R, Delsanti M (1989) Rheological properties of semidilute and concentrated aqueous solutions of cetyltrimethylammonium bromide in the presence of potassium bromide. Langmuir 5:1225–1229
- Shikata T, Hirata H, Kotaka T (1989) Micelle formation of detergent molecules in aqueous media. 3 Viscoelastic properties of aqueous cetyltrimethylammonium bromide-salicylic acid solutions. Langmuir 5:398–405
- Zhang Y, Han Y, Chu Z, He S, Zhang J, Feng Y (2013) Thermally induced structural transitions from fluids to hydrogels with pH-switchable anionic wormlike micelles. J Colloid Interface Sci 394:319–328
- 22. Han Y, Feng Y, Sun H, Li Z, Han Y, Wang H (2011) Wormlike micelles formed by sodium erucate in the presence of a tetraalkylammonium hydrotrope. J Phys Chem B 115:6893–6902
- Zhang Y, Luo Y, Wang Y, Zhang J, Feng Y (2013) Singlecomponent wormlike micellar system formed by a carboxylbetaine surfactant with C22 saturated tail. Colloid Surf A 436: 71–79
- Chu Z, Feng Y, Su X, Han Y (2010) Wormlike micelles and solution properties of a C22-tailed amidosulfobetaine surfactant. Langmuir 26:7783–7791
- Ericsson CA, Söderman O, Garamus VM, Bergström M, Ulvenlund S (2005) Effects of temperature, salt, and deuterium oxide on the self-aggregation of alkylglycosides in dilute solution. 2 *n*-Tetradecyl-β-D-maltoside. Langmuir 21:1507– 1515
- Raghavan SR, Fritz G, Kaler EW (2002) Wormlike micelles formed by synergistic self-assembly in mixtures of anionic and cationic surfactants. Langmuir 18:3797–3803
- Acharya DP, Hattori K, Sakai T, Kunieda H (2003) Phase and rheological behavior of salt-free alkyltrimethylammonium bromide/alkanoyl-N-methylethanolamine/water systems. Langmuir 19:9173–9178
- Hoffmann H, Rauscher A, Gradzielski M, Schulz SF (1992) Influence of ionic surfactants on the viscoelastic properties of zwitterionic surfactant solutions. Langmuir 8:2140–2146
- 29. Hoffmann H (1994) Structure and flow in surfactant solutions. American Chemical Society, Washington
- Lo Nostro P, Ninham BW, Ambrosi M, Fratoni L, Palma S, Allemandi D, Baglioni P (2003) Hofmeister effect in coagels of ascorbic acid based surfactants. Langmuir 19:9583–9591

- 31. (2014) http://en.wikipedia.org/wiki/Salicylic_acid. Accessed 6 Jan 2014
- 32. Zhang Y, Chu Z, Dreiss CA, Wang Y, Fei C, Feng Y (2013) Smart wormlike micelles switched by CO_2 and air. Soft Matter 9:6217–6221
- Zhang Y, Feng Y, Wang Y, Li X (2013) CO₂-switchable viscoelastic fluids based on a "pseudo" gemini surfactant. Langmuir 29:4187–4192
- 34. Rosen MJ (2004) Surfactants and interfacial phenomena. Wiley, Hoboken
- 35. Rosen MJ, Cohen AW, Dahanayake M, Hua X (1982) Relationship of structure to properties in surfactants. 10 Surface and thermodynamic properties of 2-dodecyloxypoly(ethenoxyethanol)s, $C_{12}H_{25}(OC_2H_4)_xOH$, in aqueous solution. J Phys Chem 86:541–545
- 36. Candau SJ, Oda R (2001) Linear viscoelasticity of salt-free wormlike micellar solutions. Colloid Surf A 183:5–14
- Hassan PA, Candau SJ, Kern F, Manohar C (1998) Rheology of wormlike micelles with varying hydrophobicity of the counterion. Langmuir 14:6025–6029
- Granek R, Cates ME (1992) Stress relaxation in living polymers: results from a Poisson renewal model. J Chem Phys 96:4758–4767
- Raghavan SR, Kaler EW (2001) Highly viscoelastic wormlike micellar solutions formed by cationic surfactants with long unsaturated tails. Langmuir 17:300–306
- Clausen TM, Vinson PK, Minter JR, Davis HT, Talmon Y, Miller WG (1992) Viscoelastic micellar solutions—microscopy and rheology. J Phys Chem 96:474–484

 Kern F, Lequeux F, Zana R, Candau SJ (1994) Dynamical properties of salt-free viscoelastic micellar solutions. Langmuir 10:1714–1723

Yongmin Zhang received his Ph.D. in polymer chemistry and physics from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences in 2013, and is now serving as an assistant professor at the School of Chemical and Material Engineering, Jiangnan University, People's Republic of China. His research interest lies in viscoelastic fluids and stimuli-responsive assemblies.

Dapeng Zhou earned her master's degree in applied chemistry from China Research Institute of Daily Chemical Industry in 2009, and then joined Zhejiang Zanyu Technology Co., Ltd. as an engineer. Currently, she is working on surfactants and olein chemistry.

Yujun Feng is a professor at the Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, People's Republic of China. After earning his Ph.D. in applied chemistry from the Southwest Petroleum University, China, in 1999, he moved to France performing his two post-doctoral researches at a joint laboratory of CNRS/Université de Pau and at Institut Français du Pétrole (IFP). In 2004, he returned to the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, and then to Sichuan University in September, 2012. Professor Feng has been focusing recently on self-assemblies of surfactants and amphiphilic polymers, as well as their applications in oil and gas productions.