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Introduction

Surfactants have the ability to self-assemble into a variety of microstructures including spherical, rod-like and inverted micelles, vesicles *etc.*¹ There is an increased fascinating insight into the relationship between the molecular structure of such complex fluids and their mechanical properties, which is important for the design and development of functional materials.² By now, the applications of surfactants have gone deep into many aspects of daily life and industrial products, *e.g.*, in detergent,² fracturing stimulation of oilwells,³ tertiary oil recovery,⁴ and drug delivery.⁵

The stimuli responsive surfactants have aroused considerable attention due to their particular applications. The traditional response of surfactant is usually ascribed to their stimuli-responsive functional group on the hydrophilic headgroup or the hydrophobic tail. Liu *et al.*⁶ have reported that long-chain alkyl amidine surfactant can be reversibly transformed into charged surfactant by exposure to an atmosphere of carbon dioxide, and the reaction can be reversed by bubbling N₂ or Ar. Lin *et al.*⁷ have reported the DNA complexation controlled by the cationic

Synthesis and high-performance of a new sarcosinate anionic surfactant with a long unsaturated tail[†]

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A new C_{22} tailed sarcosinate anionic surfactant, 2-(*N*-erucacyl-*N*-methyl amido) acetate (EMAA), has been synthesized by use of the erucic acid and a hydrotrope—sarcosine. In contrast to the common method, which blends the hydrotrope with a surfactant, the sarcosine has been introduced into the anionic surfactant through chemical modification. Interestingly, the resultant C_{22} tailed anionic surfactant shows excellent water solubility despite the ultra-long alkyl chain. Besides, the EMAA also exhibits high surface activity, and pH controllable micelles to vesicles transition (MVT). Rheology studies have revealed that the rheological properties of EMAA solutions are influenced by the concentration, temperature, salt, and pH dramatically. Aside from the excellent water solubility, the original feature highlighted in this work is that such a new C_{22} tailed sarcosinate anionic surfactant exhibits good temperature resistance. Compared to the potassium oleate (KOA), the zero-shear viscosity of the EMAA solution is nearly 3 orders of magnitude higher under the same conditions.

> surfactant, 1-[6-(4-phenylazo-phenoxy)-hexyl]-3-methylimidazolium bromide (AzoC6Mim). The surfactant was covalently attached with an azobenzene group, which underwent reversible photoisomerizations by changing light input, and could form an inclusion complex with α -CD through host–guest interaction. Surfactants in which the headgroup functionality or the polarity of the tail can be switched electrochemically have been reported,⁸ but they contain expensive ferrocenyl groups, highly toxic viologen groups, or groups sensitive to O₂.⁶ Most of the traditional stimuli-responsive surfactants were attained from nature, others were synthesized in a complex pathway. Therefore, the traditional stimuli-responsive surfactants were sparse. Moreover, the hydrophobic chain of which is short.

> Recently, a new system composed of surfactant and hydrotrope, has attracted considerable attention. Hydrotropes were found to provide reversible control to the formation and disruption of aggregates (such as wormlike micelles or vesicles) of surfactants in solutions, in which the surfactant interacted strongly with hydrotrope due to the electrostatic attraction and hydrophobic effect.9 Davies et al.10 have found that the cetyltrimethylammo-nium bromide/5-methyl salicylic acid (5mS) would form unila-mellar vesicles in aqueous solutions. When these vesicles were heated above a critical temperature, they transformed into long, flexible wormlike micelles. Ketner et al.11 have reported a photorheological fluids system composed of cetyl trimethylamm-onium bromide (CTAB) and trans-orthomethoxycinnamic acid (OMCA). Upon irradiation by UV light (<400 nm), OMCA under-went a photoisomerization from its trans to its cis form, resulted in the transformation of long

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micelles into much shorter entities. Wang *et al.*¹² have reported a complex aqueous solution composed of tetradecyldimethylamine oxide and *para*-coumaric acid. And a phase transition from vesicles to wormlike micelles performed *via* UV-light irradiation. The preparation of this blended system is simple.

It should be noted the aforementioned functional surfactants reported were mainly focused on the cationic surfactants which bearing a $C_{12} \sim C_{16}$ tail. However, recent studies have revealed that the anionic surfactants would show some better performances compared to its cationic counterpart. For example, cationic surfactants were severely restricted in their application in enhanced oil recovery, due to the negative charges of oil sand. Also, it has been demonstrated that anionic surfactant was more biodegradable and less toxic bahaviour. Besides, not only is the long tailed anionic surfactant barely investigated,¹³ there have some problems in the existing anionic surfactant systems. To ensure the water solubility, the reported anionic surfactants to date were mainly focused on a C18 tail and below.14 Furthermore, these reported anionic surfactants showed bad temperature resistance, that is, at room temperature their viscosities could reach high values, but at higher temperatures the high viscosities could not be maintained. Therefore, strengthening investigation on the anionic surfactant especially the long tailed anionic surfactant is necessary for their potential applications in many fields.

Inspired by the previous work, we wonder what new properties may generate if the hydrotrope is introduced into the anionic surfactant headgroup through chemical modification, not physical blend. Here, we report a new C222 tailed sarcosinate safactant, EMAA, can be obtained easily by the combination of the erucic acid and a hydrotrope, sarcosine. It is already known that the sodium erucate cannot dissolve in water unless the temperature is higher than 60 °C.15 It was mixed with the choline to promote the formation of wormlike micelles as shown by Han et al.16 However, temperature was still needed to be higher than 50 °C to solubilize the surfactant. Of peculiar interest is that once the hydrotrope is introduced into the anionic surfactant headgroup by means of chemical modification, EMAA can dissolve in water at room temperature and no opaque appears when the temperature drops to 0 °C. That is to say, EMAA has excellent solubility despite the ultra-long alkyl chain (C22 tail). Moreover, the EMAA also exhibits high surface activity, and pH controllable MVT at room temperature in which the sodium erucate lacked. Of practical relevance to construct high-performance surfactant, the EMAA has also shown attractive rheological property and better temperature resistance. Especially, compared to the potassium oleate (KOA), the zero-shear viscosity of the EMAA solution is nearly 3 orders of magnitude higher under the same conditions.

Experimental

1. Materials

Potassium hydroxide, potassium chloride, phosphorus trichloride, sodium hydroxide, concentrated hydrochloric acid, ethyl acetate, petroleum ether (30 $^{\circ}$ C–60 $^{\circ}$ C), erucic acid and sarcosine were all of analytical grade, purchased from sinopharm

$$R - C_{8}H_{17} - CH = CH - C_{11}H_{22} - CH - C_{11}H_{22} - CH = CH - C_{11}H_{22} - CH - C_{11}H_{22} - CH = CH - C_{11}H_{22} - CH - C_{11}$$

Scheme 1 Synthesis pathway for erucacyl chloride.

and used as received. All solutions were prepared in distilled water. The pH was determined by a Shengci PHS-3C pH meter.

2. Preparation of EMAA

2.1. Preparation of erucacyl chloride. Erucic acid (75.00 g, Mw = 338.57 g mol⁻¹, 0.2215 mol) was introduced into a well-stirred four-necked flask equipped with thermometer and reflux condenser. Phosphorus trichloride (19.85 g, Mw = 137.33 g mol⁻¹, 0.1445 mol) was added dropwise. The reaction mixture was refluxed at 78 ± 0.5 °C for 3 h. Precipitate was filtered from the solution. The synthetic procedure is outlined in Scheme 1.

2.2. Preparation of 2-(N-erucacyl-N-methyl amido) acetate. Sodium sarcosinate (18.90 g, $Mw = 111.08 \text{ g mol}^{-1}$, 0.1702 mol) and 282 mL water were introduced into a well-stirred four-necked flask equipped with thermometer. erucacyl chloride (52.6 g, Mw $= 357.07 \text{ g mol}^{-1}$, 0.1473 mol) and 10% sodium hydroxide was added dropwise synchronously. The solution was kept in the pH range of 9-11, and the temperature range of 30 °C-35 °C. After the addition was completed the reaction was continued for another 1 h, during which the by-product HCl was neutralized continuously by sodium hydroxide. Afterwards, the solution was acidified with concentrated hydrochloric acid slowly to a pH below 3 and extracted with ethyl acetate. The extracts were washed with distilled water to neutrality and then dried over anhydrous sodium sulfate. The solvent was removed by reduced pressure distillation. The residue was recrystallized from petroleum ether (30 °C-60 °C) and freeze-dried. The synthetic procedure is outlined in Scheme 2. The structures confirmed by elemental analysis (Vario EL cube elementar made in Germeny), infrared (IR, Perkin Elmer spectrum 100 USA), ¹H nuclear magnetic resonance (¹H NMR) spectroscopy and ¹³C NMR spectroscopy (ESI Table 1, Fig. 1–3[†]). The ¹H NMR data were obtained from an AC400 Bruker spectrometer operated at 400 MHz and 100 MHz for ¹³C NMR. Here, we give the ¹H NMR data. The peak appearing at 7.25 ppm belongs to solvent peak of CDCl₃, and 0 ppm belongs to TMS. ¹H NMR (400 MHz, CDCl3) $\delta = 8.89$ (s, 1H, COOH), 5.43–5.28 (m, 2H, -HC=CH-), 4.14 (d, J = 33.3 Hz, 2H, N-CH₂-), 3.09 (d, J = 43.8 Hz, 3H, N-CH₃), 2.37-2.13 (m, 2H, -CH₂CO-), 2.11-1.77 (m, 4H, -C=C-CH₂-), 1.72-1.54 (m, 2H, -CO-CH2-CH2-), 1.28 (s, 28H, H3C-(CH2)6, -CH2-CH=CH- CH_2 -(CH_2)8- CH_2 -), 0.88 (t, J = 6.9 Hz, 3H, H_3C -).

3. Surface tension measurements

Surface tensions (γ) of aqueous EMAA solutions were measured with a KSV minithrough equipment (KSV, Helsinski, Finland). Series of measurements were taken at 10 min intervals until the change in surface tension was less than 0.05 mN m⁻¹, and all the measurement accomplished at 25 °C. The cmc and the corresponding surface tension were determined from the

$$\begin{array}{c} O & CH_3 \\ \parallel & \parallel \\ R - CC1 + HN - CH_2 - COOH \xrightarrow{30 \sim 35^{\circ}C} & O & CH_3 \\ \hline & & & \\ OH^- & & \\ \end{array} R - C - N - CH_2 - COO^- \quad (2)$$

Scheme 2 Synthesis pathway for 2-(*N*-erucacyl-*N*-methyl amido) acetate.

breakpoint of the curve of surface tension *versus* the logarithm of the concentration.

4. Dimension measurements

The dimension measurement was accomplished with a temperature-controlled Zetasizer Nano instrument (Zetasizer nano ZS, Malvern). The temperature during measurement fixed at 25 $^{\circ}$ C, and before measurement every sample underwent an equilibrium for 30 s.

5. TEM observation

The TEM observation was accomplished with a JEM-2100 high resolution transmission electron microscope, and the acceleration voltage was 200 kV. The concentration is fixed at 0.5 mg mL⁻¹.

6. Rheology

The rheology experiment was carried out on a stress-controlled rheometer (TA-AR-G2, America) using a concentric cylinder geometry with a measuring rotor radius of 14 mm and a measuring cup radius of 15 mm. Except as noted, all measurements were performed at 25.0 ± 0.1 °C. The viscosities of the samples were obtained from steady-shear measurements with the shear rate ranging from 0.001 to 100 s⁻¹, and all underwent a pre-shear operation for 5 minutes at 10^{-5} s⁻¹. Frequency sweep measurements were performed at a given stress σ_0 (0.01 Pa, chosen in the linear domain where the amplitude of the deformations is very low).

Results and discussion

1. Solubility

It is no doubt that solubility or homogeneity of the sample is the primary consideration for further examination.14 The temperature at which the solubility of ionic surfactants rises sharply is known as the Krafft point (T_K) , where the solubility of the surfactant is normally equal to its cmc.¹⁷ Above $T_{\rm K}$, the surfactant is soluble in water independent of its concentration.¹⁸ The $T_{\rm K}$ of the surfactant generally increases with lengthening its hydrophobic chain and decreases with the introduction of an unsaturated bond onto the tail and enlarging hydrophilic headgroup. Generally speaking, the surfactant with ultra-long hydrophobic tail exhibits a high $T_{\rm K}$. For example, the aqueous sodium erucate solutions of 100 mM were prepared at 60 °C.15 Zhang et al. reported a saturated C22-tailed surfactant-docosyldimethyl carboxylbetaine (DDCB) had a T_K of 59.5 °C.¹⁹ The 3-(N-erucamidopropyl-N,N-dimethyl ammoniu-m) propane sulfonate could not be dissolved even in boiling water, which means that its $T_{\rm K}$ is higher than 100 °C.¹⁴ And homogeny-eous surfactant solutions of 70 mM NaOEr and a designed amount appropriate hydrotropic salt were obtained by dissolving at 50 °C.²⁰ The solution mixture of choline chloride and NaOEr of 100 mM was kept in a water bath at 50 °C for at least 24 h to ensure equilibration.¹⁵ These C₂₂ tailed surfactants all have headachy solubility.

However, we can attain the aqueous EMAA solution of 200 mM at room temperature, and no opaque appears when the temperature is decreased to 0 $^{\circ}$ C. As mentioned above, the $T_{\rm K}$ of EMAA is below 0 °C. As to the solubility of aqueous EMAA solution, which is influenced by the three aspects of molecular structure: (a) EMAA bears a long hydrophobic tail; (b) the hydrophobic chain is unsaturated; and (c) the large hydrophilic headgroup is a sarcosinate. Being aware of these points, it is not hard to understand the peculiarity of these parameters with respect to EMAA. It is well known that $T_{\rm K}$ of the surfactant increases upon lengthening its hydrophobic tail. Negative charged hydrophilic headgroup has a strong ionic hydration, thus the solubility increases, which leads to a decrease of $T_{\rm K}$. Moreover, EMAA has a big hydrophilic headgroup and an unsaturated hydrophobic chain. They induce the increase of solubility, lead to a further decrease of $T_{\rm K}$. Compared with other C22 tailed surfactants, the good solubility of EMAA must endow which a better application potential.

In addition, the low $T_{\rm K}$ results in low cmc. As shown in Fig. 1, the cmc and the corresponding surface tension are determined from the breakpoint in the surface tension versus logarithm of surfactant concentration plot. The breakpoint value is -4.25, that is to say the cmc is 5.62×10^{-5} mol L⁻¹ and the corresponding surface tension is 27.2 mN m^{-1} . This may be due to the strong hydrophobic interaction of C22 long alkyl chain. Because of the formation of micelles is the equilibrium of two interactions, one is hydrophobic interaction favoring to form micelles resulted from long alkyl chain, the other is electrostatic repulsive interaction which prevents the formation and growth of micelles resulted from the ionized headgroup.²¹ Therefore, longer alkyl chain will induce stronger hydrophobic attraction, micelles are easier to form, which results in lower cmc and surface tension. EMAA possesses high surface activity, which will lead to a huge potential in life and industry application.



Fig. 1 Variation of surface tension *versus* the logarithm of the concentration of EMAA.

2. Micelle-vesicle transition induced by pH

As we can see, Fig. 2 displays the size analysis of the aggregates in solution containing 30 mM EMAA at various pH. There are two peaks in the plot and the average diameter are 2.3 nm and 25 nm respectively at the pH 10.09, the inset shows a colorless and transparent solution. This can be explained by the coexistence of spherical micelles and rodlike micelles.²² However, the situation became different as the pH decreased to 6.77, the peak corresponding to the small aggregates (~10 nm) shrinks, the solution begins to turn bluish, and the two peaks move right along x-axis distinctly, this proves the growth of the aggregates. As the pH decreases to 6.50, the plot shows a single peak and the average diameter of 67.28 nm, the inset shows a strong bluish color. Based on the previous work, the bluish color exhibited by the cloudy and opaque solution is attributed to the Tyndall effect, which is typical for a solution containing a large aggregate-like vesicles.23 This solution may be the coexistence of rodlike micelles and vesicles.²³ When the pH is 5.52 the peak goes on moving right, and the single peak splits to doublet, which is indicative of the increase in the vesicle/micelle ratio in the system. As the pH decreases to 4.49, the peak at left is weakened and the right peak is strengthened, the solution displays bluish still, but turns more opaque. This proves the coexistence of rodlike micelles and vesicles and the growth of vesicles again. We can deduce that with the pH dropping the micelles will turn into vesicles completely. Therefore, the EMAA solution exists a MVT with the variation of pH. The mechanism for this transition (which occurs for all long-chain fatty acids) has been discussed in a number of studies, and the central factor is believed to be the change in the degree of ionization of



Fig. 2 Diameter sizes of the aggregates at various pH values in the 30 mM EMAA solution.



Fig. 3 TEM photographs of EMAA solution in different pH: 3.59 (the left), 7.57 (the middle) and 11.29 (the right). And the concentration is fixed at 0.5 mg mL⁻¹.



Scheme 3 The transformation between vesicle and micelle induced by pH.

the fatty acids.²⁴ The MVT can be proved by the TEM photographs in Fig. 3. The picture on the left shows typical vesicles dimensions, the middle one shows a state with major spherical micelles, and the right one exhibits the existence of linear micelles.

For the MVT, the theory of surfactant packing parameter R_p can give a reasonable interpretation. And Scheme 3 shows the MVT process. R_p is defined *via* the formula of

$$R_{\rm p} = \frac{V_0}{A_{\rm h} \times L_0} \tag{1}$$

where $A_{\rm h}$ is the area at the effective micellar surface of surfactant headgroup(s), and L_0 and V_0 are the length and volume of completely extended hydrophobic tail(s). $R_{\rm p}$ is a fundamental quantity to forecast possible micellar aggregation shapes. When $R_{\rm p} < 1/3$, spherical micelles are formed; when $1/3 < R_{\rm p} < 1/2$, WLMs are found; and when $1/2 < R_{\rm p} < 1$, vesicles or bilayers can be obtained. With dropping the pH, anionic headgroups COO⁻ are replaced by the nonionic headgroups COOH gradually. The electrostatic repulsions interactions among negative charged headgroup turn weak, resulting in a decrease in $A_{\rm h}$ and a corresponding increase in $R_{\rm p}$. Therefore, the MVT undergoing the process of spherical micelles, rod-like micelles and vesicles is consistent with the theory.

At high pH, the carboxylate groups on EMAA are fully ionized, and the head groups of the amphiphile thus bear a strong negative charge. The repulsions of these head groups lead to the formation of spherical micelles. Because the micelle size is only around 5 nm, the solutions scatter light weakly and therefore appears transparently. When the pH is lowered to a value close to the pK_a , approximately half the EMAA groups are no longer ionized. The charge may then be considered to be shared by two adjacent fatty acid molecules, one ionized and the other unionized: *i.e.*, the molecules are effectively paired into dimers. The net amphiphile geometry then becomes conducive to formation of vesicles rather than micelles. The vesicles typically range from 50 to 150 nm in diameter (much larger than the micelles), and therefore the solutions scatter light strongly, leading to the bluish color.

3. Effect of pH on rheological behaviour

The pH switchable property was confirmed by the rheological measurement of the solution containing 50 mM EMAA and 3% KCl. Fig. 4a shows the variation of steady shear viscosity (η) as a function of shear rate at different pH values (changing from 6.43 to 13.04) and the temperature was fixed at 25 °C. Zero-shear viscosity (η_0) of the solution is obtained by extrapolation of the shear viscosity along the Newtonian plateau to zero-shear rate.

All rheograms show a Newtonian plateau at low shear rates and a shear-thinning slope when the shear rate reaches a critical value, indicative of the presence of WLMs.²⁵ When the pH is 6.43, the value of zero shear viscosity of the solution is very small about 3–4 Pa s, and the aqueous EMAA solution presents opaque as the inset is displayed in Fig. 4b. When the solution turns alkaline, it turns transparent immediately, and viscosity rises sharply. As shown in Fig. 4b, when pH rises from 6.43 to 7.36, η_0 rises from 3.8 to 222.5 Pa s. And the solution can support its own weight when pH increases to 9.50, as the inset represents in Fig. 4b, shows excellent viscoelastic properties. Then the zero shear viscosities rise slowly. The zero shear viscosities are hardly changed after the pH is raised to 10.57. As presented in Fig. 4b, the last part of the curve of zero shear



Fig. 4 Effect of pH on (a) steady rheology, (b) zero-shear viscosity of the solution containing 50 mM EMAA and 3% KCl. (T = 25 °C).



Fig. 5 The structural models of isomers of EMAA



Scheme 4 The transition process from spherical micelles to wormlike micelles with increasing pH or surfactant concentration.

viscosity presents a plateau. For the zero shear viscosities raised with pH, the theory of surfactant packing parameter R_p can give a reasonable interpretation.

In our current work, when the solution is acidic, the headgroup of COOH is predominant in quantitative terms. With the pH rising, anionic headgroups COO⁻ replace the nonionic headgroups gradually. EMAA exists two isomers and the structures are exhibited in Fig. 5 (the trans and cis conformations, cis/ trans ratio of amide is 1/5 according to the peak intensity of the ¹³C NMR and ¹H NMR spectroscopy in CDCl₃ (SI Fig. 2 and 3[†])). Trans isomers of the type surfactants are more stable in the micelle state because they have smaller cross sections relative to their cis isomers,26,27 which results in EMAA-trans isomer will increase during the formation of micelles. The micelles grow gradually with pH increasing. So, the trans/cis ratio will increase with pH increasing. The A_h will decrease with trans/cis ratio increasing, which result the increase of $R_{\rm p}$. Due to the existence of 3% KCl, K⁺ compresses the hydration layer of surfactant headgroups and the electric double layers of micelles by the strong electrostatic interactions with the anionic surfactant headgroups, resulting in a further decrease in A_h and a corresponding increase in $R_{\rm p}$. Consequently, the pH promotes the growth of micelles, corresponding to the pH changing from 6.43 to 10.57. When the pH goes on rising, zero shear viscosity hardly increases, this is owing to that all headgroups COOH of the surfactant turn to COO⁻, the pH has little influence on A_h. The process displayed in Scheme 4.

4. Effect of KCl concentration on rheology behavior

Here we investigate the effect of KCl concentration on steadystate rheology of 50 mM EMAA solution with pH fixed between 10.57 and 13.04, to ensure the optimal pH effect. In Fig. 6a, it is clearly shown that all rheograms composed of a Newtonian



Fig. 6 Effect of KCl concentration on (a) steady shear viscosity and (b) zero shear viscosity and (c) dynamic rheology of the solution containing 50 mM EMAA.

plateau in low shear rate range and a shear thinning slope in high shear rate range. The viscosity drops rapidly due to the breakage of wormlike micelles, which confirms the existence of WLMs again as aforementioned. And with raising KCl concentration the Newtonian plateaus are shortenned and the zero shear viscosities increase.

Zero-shear viscosities (η_0) are plotted as a function of KCl concentration values to examine the effect of KCl concentration on viscosity. The viscosities increase quickly with KCl concentration increasing from 0 to 7%, however after the concentration reaches 8% the zero shear viscosity drops surprised as we can see from Fig. 6b. The growth process of micelles displayed

in Scheme 4, scattered sphere micelles existing in solution begin to combine and grow into rodlike micelles which lead to the increase of the viscosity with adding KCl, then the lengths of rodlike micelles increases further, they become linear and entangle together to form a dense network and results in a rapid increase in viscosity. However, too much K⁺ adsorbs on the micelles surface which may further reduces the electrostatic repulsion and the linear micelles may become huddled. Ultimately the micelles undergo a transition from linear ones to branched ones whose framework is a little weaker than the linear micelles. The relaxation of mechanical stresses in such a system occurs by sliding of branching points along the micellar chains.28 This process requires low energy consumption, the viscosity of the system decreases. Finally, at very high salt concentrations of 11% KCl, the system phase separates into a concentrated, highly branched or liquid crystal phase and a dilute phase. Compared with sodium erucate-choline system, the addition of inorganic salt KCl can obtain the same effect on viscosity. However, it is unfavorable for choline to penetrate the micelle because of the repulsive interaction between the hydrophilic -OH and the hydrophobic hydrocarbon tail of the surfactant.29

The KCl concentration dependence of the viscoelasticity of 50 mM EMAA micellar system is shown in Fig. 6c where the storage modulus (G') and loss modulus (G'') are plotted as functions of oscillatory shear frequency (ω) at 25 °C and different KCl concentration values. At the KCl concentration of 1%, G' crosses and prevails over G'' when exceeding a critical shear frequency (ω_c) at around 0.0155 rad s⁻¹. Obviously, the solution presents a typical elastic response, and at low shear frequency the solution displays an evident viscosity behavior. That is to say, relaxation time (τ_R) is finite for EMAA solution. Upon increasing KCl concentration the plateau modulus G_0 (storage modulus at high frequencies) increases, this may be due to that more KCl lead to strong screening of electrostatic repulsion and the growth and entanglement of micelles to form a dense network of WLMs. Furthermore, when KCl concentration exceeding 2% in the high-viscosity region, G' always exceeds G" over the whole frequency range examined, showing very strong elastic behaviors. In this case, although the ω_c is too low to be determined, one can deduce that G' will cross over and drop below G'' at a lower ω , and an approximate $\tau_{\rm R}$ can be obtained by the following equation for further comparison:

$$\tau_{\rm R} = \frac{\eta_0}{G_0} \tag{2}$$

The G' still increase when the KCl concentration is 9%, which is mainly owing to the formation of branched WLMs which possess high elastic, though the viscosity is reduced.

The viscoelastic behavior of wormlike micelles solution as a Maxwell fluid with single relaxation time and variation of the storage modulus G' and loss Modulus G'' as a function of oscillatory frequency ω is described by the following relations:

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

where $\tau_{\rm R}$ is the relaxation time which can be estimated by eqn (2). In Fig. 5c, the solid line represents the theory value of G' and G''. As shown, the EMAA solution can agree with Maxwell model except slope of G'' in high shear frequency. Indicating a typical visco-elastic fluids behavior with a single relaxation time dominates the response, which verifies the presence of WLMs again. While the deviation of G'' from Maxwell model can usually be interpreted as a transition in relaxation mode from reptation at longer time scales to "breathing" or rouse mode at short time scales.³⁰

5. Effect of the EMAA concentrations on rheological property

The effect of surfactant concentration on rheological property of the solution is a basic study, and the influence was represented. In Fig. 7a, a series of rheograms at different EMAA concentrations have been plotted. All samples contain 7% KCl and fix the pH between 10.57 and 13.04, to ensure the optimal effect. Obviously, with increasing the EMAA concentration, the shear viscosity increases, which is only 6.51 Pa s at the concentration of 10 mM, 2941 Pa s at 100 mM which is 7 orders of magnitude higher than water at 25 °C. This is a very excellent property compared with many long-tailed or gemini surfactants.

As displayed in Fig. 7b, the storage modulus (G') and loss modulus (G') were plotted as a function of oscillatory shear

frequency (ω) at 25 °C at the EMAA concentration of 10 mM and 20 mM respectively. It can be seen clearly that with increasing the concentration of EMAA G' and G'' increase. G' always exceeds G'' over the whole examined frequency range, showing very strong elastic behaviors. The ω_c is too low to be determined, however one can deduce that G' will cross over and drop below G'' due to the finite relaxation time of this system.

6. Effect of temperature on rheology behaviour

Temperature is one of the most important factors determining solution properties; moreover, the practical applications of micellar solutions are usually confined at given temperatures. Therefore it is necessary to investigate the influence of temperature on the micellar system formed in this work. Fig. 8a shows the steady rheological responses for the sample containing 100 mM EMAA and 7% KCl in the temperature range of 25-90 °C. As shown, with raising the temperature, the shear viscosity drops from 2941 Pa s at 25 °C to 4.0 Pa s at 90 °C, indicating an evident temperature influence. The influence of temperature on viscosity is due to the decreased average micelle length upon increasing temperature.³¹ It is worth noting that η_0 is still >10³ mPa s at 90 °C, which suggests the good stability of the entangled micelles at high temperature. This can be attributed to the long breaking time of the micelles because of the long hydrophobic tail attached on the surfactants.³² With the zero shear viscosity decreasing, the Newtonian plateau turns



Fig. 7 Effect of the EMAA concentration on (a) steady-state shear (b) dynamic rheology of EMAA solution with 7% KCl.



Fig. 8 (a) Effect of temperature on rheology of the solution containing 100 mM EMAA and 7% KCl. (b) Comparison of shear viscosities of potassium EMAA with potassium oleate (100 mM and 7% KCl) at 25 °C and 90 °C.

longer. So the viscosity at 25 °C is higher than that at 45 °C according to this law, due to the Newtonian plateau of 25 °C is shorter than that at 45 °C. However, the influence of temperature on EMAA solubility is little, so the surfactant has an excellent potential application at various temperatures.

As shown in Fig. 8b, the comparison is evident that the viscosity of potassium EMAA is 3 orders of magnitude higher than that of potassium oleate, and the values are 2941 Pa s and 1.09 Pa s at 25 °C; 4.0 Pa s and 2.0×10^{-3} Pa s at 90 °C respectively. EMAA has more prominent rheological property than the latter, indicating the former has better prospect in industrial and daily life application. Of course, these may be due to potassium EMAA has longer hydrophobic hydrocarbon chain. The length of surfactant tails has important influence on the rheological properties of their solutions. However, the longer hydrocarbon chain may result in poor solubility in water. Compared with other surfactant of same kind, the property of dissolving in water easily is an important advantage in practical application.

Conclusion

In conclusion, a new C₂₂ tailed sarcosinate anionic surfactant, 2-(N-erucacyl-N-methyl amido) acetate (EMAA), has been synthesized by use of the erucic acid and a hydrotrope-sarcosine. Unlike the common method, which blends the hydrotrope with surfactant physically, the hydrotrope here has been introduced into the anionic surfactant through a simple synthetic method. The resultant C222 tailed anionic surfactant shows expected high performance, i.e., high surface activity, pHcontrollable MVT, excellent rheological property and good temperature resistance. Furthermore, the C₂₂ tailed anionic surfactant shows unusual excellent water solubility despite the ultra-long alkyl chain (C_{22}). Thus, a simple strategy is proposed to design and fabricate high-performance surfactant by combination of the surfactant and the hydrotrope, which will lead to the multiplied effects, that is to say, contributing to the practical application of surfactant, and providing a universal strategy for designing high-performance material.

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