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Phase Behavior and Rheological Properties of a Salt-Free Catanionic Surfactant TTAOH/LA/H₂O System

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Received: March 14, 2008; Revised Manuscript Received: June 4, 2008

Conventional cationic and anionic (catanionic) surfactant mixtures tend to form precipitates at the mixing molar ratio of the cationic and anionic surfactant of 1:1 because of the excess salt formed by their counterions. By using OH[−] and H⁺ as the counterions, however, excess salt can be eliminated, and salt-free catanionic systems can be obtained. Here, we report the detailed phase behavior and rheological properties of salt-free catanionic surfactant system of tetradecyltrimethylammonium hydroxide (TTAOH)/lauric acid (LA)/H₂O. With the variation of mixing molar ratio of LA to TTAOH ($\rho = n_{\text{LA}}/n_{\text{TTAOH}}$), the system exhibits much richer phase behavior induced by growth and transition of aggregates. Correspondingly, the rheological property of the system changes significantly. Take the series of samples with fixed total surfactant concentration (c_{T}) to be 15 mg·mL^{−1}, the system only forms a low viscous L₁ phase with a Newton fluid character at the TTAOH-rich side. With increasing ρ , first a shear-thickening L₁ phase region is observed at $0.70 \leq \rho \leq 0.80$, and then the system reaches a viscoelastic L₁ phase region at $0.80 < \rho < 0.88$, which exhibits Maxwell fluid character. With further increasing ρ , an L₁/L _{α} two-phase region reaches with birefringent L _{α} phase at the top, and after that a bluish vesicle phase is observed at $0.92 < \rho < 1.05$. At the LA-rich side, phase separation of the bluish vesicle phase occurs at $\rho \geq 1.05$, and finally, at $\rho \geq 1.13$, the excess LA will separate from the bulk solution and form a white top layer. Investigations were also carried out by varying c_{T} at fixed ρ and by changing temperature, respectively. It was found micelle growth would be greatly suppressed at higher temperatures. However, the vesicle phases showed a considerable resistance against temperature rise.

Introduction

Surfactants which possess hydrophobic and hydrophilic properties can self-assemble to complicated aggregates in solutions. In both fundamental research and practical applications, mixed surfactant systems are frequently selected rather than single components. Cationic and anionic (catanionic) surfactant mixtures were known to form thermodynamically stable vesicles in dilute aqueous solutions, as discovered by Kaler et al. in 1989.¹ After that, a flame on the study of catanionic surfactant mixtures was triggered during the following years.^{2–9} With variation of mixing ratio, these systems showed much richer phase behavior induced by phase structure transition from globular micelles to rod-like micelles or worm-like micelles and vesicles. Of course, different mesophase structures were reported. Also observed were interesting two-phase or multiphase regions, which usually appeared between worm-like micelles and vesicles. For most investigated catanionic surfactant mixtures, however, precipitates were often observed, especially when the stoichiometry between cationic and anionic surfactant was exactly 1.¹⁰ This was mainly ascribed to the existence of excess salt formed by the counterions. The existence of salts, or more precisely, the small counterions, induces a high ionic strength and screens the electrostatic interactions between aggregates, making the system unstable.

By suitable sample treatments such as extraction and dialysis, salt-free catanionic systems can be obtained.^{11–14} During the past 10 years, a renewed interest has been devoted to the study of salt-free catanionic systems, and novel methodologies have been

found to eliminate the excess small counterions. Good work has been done by several research groups in this respect, especially those led by Hoffmann, Zemb, and Hao, respectively.^{10,15–30} Typically, two methods are adopted to prepare salt-free catanionic systems: (a) by mixing aqueous solution of alkyldimethylamine oxide with divalent metal ionic surfactants^{14–17} or acids typically with a hydrophobic long tail^{19–22} and (b) by mixing alkyltrimethylammonium hydroxide with fatty acids in water.^{23–30} In the former case, metal ions such as Zn²⁺, Ca²⁺, and Ba²⁺ etc. were believed to be fixed at the membrane of aggregates through the formation of metal–ligands with the headgroup of alkyldimethylamine oxide, leaving the system salt-free. In the latter case, the counterions were eliminated partially (in case of nonequimolar) or totally (in case of equimolar) because OH[−] reacts with H⁺ to form water. Because of no excess salt, the conductivity and ionic strength of salt-free catanionic systems are extremely low when the stoichiometry between cationic and anionic surfactant is exactly 1. The electrostatic interactions between aggregates are thus unscreened, and the osmotic pressure of the aggregates was very high, which was believed to be the factor dominating the stability of the system.^{27,28} For this reason, salt-free catanionic systems can be prepared at much higher concentrations without precipitates at the stoichiometric point compared to salt-containing catanionic systems, and a bluish phase or birefringent L _{α} phase was usually observed. This provided great potential applications for salt-free catanionic systems and was really the point on which most published work has focused. Investigations have revealed that the birefringent L _{α} phase usually contains densely packed uni- and multilamellar vesicles or lamellar phases.^{15–26} Recent studies on the system

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of cetyltrimethylammonium hydroxide (CTAOH)/myristic acid (MA)/H₂O also revealed the formation of interesting disk-like micelles on the CTAOH-rich side, and regular hollow icosahedra on the MA-rich side.^{27–30}

In most published work on salt-free catanionic systems, usually only a simplified phase diagram obtained by fixing the concentration of cationic surfactant and increasing the amount of anionic surfactant was given. A well-defined pseudoternary phase diagram depicting the detailed aggregate transition as a function of mixing ratio and total surfactant concentration is still unavailable. The rheological properties of different phases formed by salt-free catanionic systems especially for the rod-like and worm-like micelles have not been well described yet. To overcome these shortcomings, we report in this paper the detailed phase behavior and rheological properties of salt-free catanionic system of tetradecyltrimethyl ammonium hydroxide (TTAOH)/lauric acid (LA)/H₂O. With variation of the mixing molar ratio of LA to TTAOH (ρ) and total surfactant concentration (c_T), the system shows much richer phase behavior at 25 °C. The rheological properties of the shear-thickening rod-like micelles, the viscoelastic worm-like micelles, and the gel-like densely packed vesicles were investigated in detail as a function of concentration and temperature. Surface tension measurements were carried out for dilute solutions on the TTAOH-rich side to clarify the strong ion-pairing between TTAOH and LA. The interesting L_1/L_α two-phase region was also investigated by means of rheological measurements and polarized microscopy observations. Our study provides rather detailed data, which should be helpful not only for a deeper and comprehensive understanding of salt-free catanionic systems, but also for further broadening the potential applications of salt-free catanionic systems.^{31,32}

Experimental Section

Chemicals and Materials. LA (chemical grade, >98%) was purchased from Shanghai Shiyi Chemicals Reagent Co. Ltd. and used without further purification. TTAOH stock solution was prepared from a trimethylammonium bromide (TTABr; Merck, analytical grade, used without further purification) aqueous solution by anion exchange (Ion exchanger III, Merck) following procedures described previously.^{24–26,31,32} The concentration was determined by acid–base titration by using standard HCl aqueous solution. Because a small amount of white crystals or precipitates were usually seen at the bottom of the TTAOH stock solution after long time storage, TTAOH stock solution was freshly prepared for each sample preparation process, and its concentration was determined by using the same standard HCl aqueous solution to minimize experimental errors. Water used in the experiments was triply distilled by a quartz water purification system.

Phase Behavior Study. Phase behavior was studied by visual inspection and with the help of crossed polarizers. Two methods were adopted to prepare samples: (a) Several series of samples, each having the same c_T but varying ρ , were designed. In brief, to an empty bottle a desired amount of TTAOH stock solution and solid LA was added. The final volume was adjusted to the same value by adding water. On the TTAOH-rich side, LA dissolved easily. With increasing ρ , however, it became difficult for the water-insoluble LA to dissolve totally, especially when $\rho > 1$. So heating to ~ 60 °C and frequent shaking was performed on these samples to get homogeneous solutions. After that, the samples were kept at 25 °C for at least four weeks before phase behavior was inspected. (b) After Method a, several series of samples, each having the same ρ but varying c_T , were

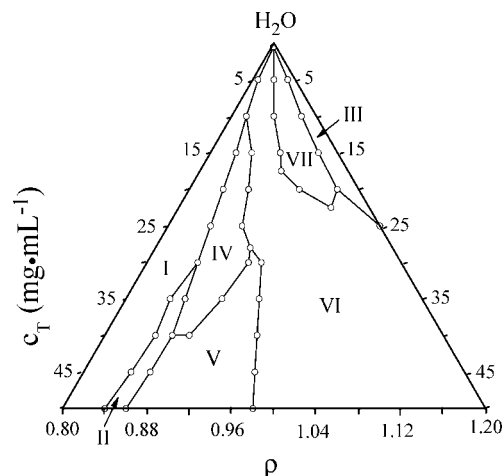


Figure 1. Water-rich corner of pseudoternary phase diagram for TTAOH/LA/H₂O at 25 °C. I: L_1 phase (micellar phase). II: L_1 phase with precipitates at the bottom. III: white precipitates were observed at the top layer. The bottom phase is colorless at low concentrations and bluish at higher concentrations. IV: L_1/L_α two-phase region with birefringent L_α phase at the top. At higher concentrations, white precipitates were observed, which tend to distribute near the phase boundary. V: single birefringent L_α phase. White precipitates were frequently seen, which tend to deposit at the bottom or suspend in the bulk solution. VI: bluish vesicular phase. VII: the bluish vesicular phase separated into two phases.

also designed. In brief, stock solutions with different ρ were first prepared according to Method a, which were then dried below 50 °C with the help of an oven to obtain solid surfactant mixtures. A desired amount of each solid surfactant mixture was then weighed accurately into test tubes, and the final volume was adjusted to the same value by water. Within the first several days, gentle shaking was performed on each sample to accelerate the dissolution process of solid surfactant mixture. Then the samples were kept at 25 °C for at least four weeks before phase behavior was inspected.

Now we have gained a general knowledge about the phase sequence for a TTAOH/LA/H₂O system as a function of c_T and ρ . Further studies were carried out with preparing additional samples to determine phase boundaries more precisely. The highest value of c_T and ρ for the samples in our experiments are 60 mg·mL⁻¹ and 1.363, respectively. The final pseudoternary phase diagram given in Figure 1 was the result of the observation for more than 150 samples.

Rheological Measurements. Rheological measurements were carried out on a HAAKE RS75 Rheometer with a coaxial cylinder sensor system (Z41 Ti). In steady shear experiments, the shear rate was typically increased from ~ 0.2 s⁻¹ to 1000 s⁻¹ within 5 min. In oscillatory measurements, an amplitude sweep at a fixed frequency of 1 Hz was performed prior to the following frequency sweep in order to ensure the selected stress was in linear viscoelastic region. In experiments aiming to see temperature influence, temperature was typically increased from 25 to 60 °C with the help of a cyclic water bath (Phoenix). The gap of temperature rise was 5 °C. After each temperature rise, the sample was allowed to equilibrate for an additional 5 min before measurements.

The volume of each sample used for measurements was usually 25 mL. Because samples within and around the worm-like micelle region have strong Weissenberg rod-climbing effect, the volume of each sample was increased or the highest shear rate in steady shear measurements was reduced in order to avoid samples climbing out of the gap of the coaxial cylinder.

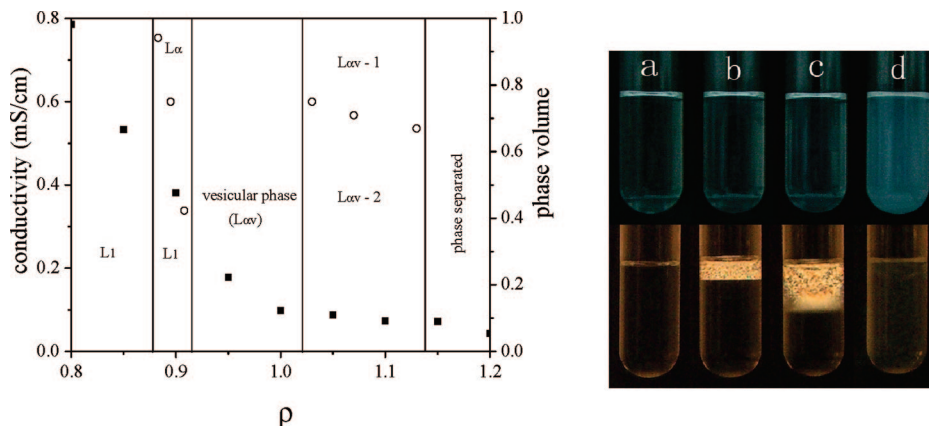


Figure 2. Left: A section of pseudoternary phase diagram with $c_T = 15 \text{ mg} \cdot \text{mL}^{-1}$. The conductivity data (■) and phase volume ratio (○) within the two-phase regions were also given. The conductivity data within the two-phase regions were measured before phase separation. Right: Photos of four typical samples at different regions without (top) and with (bottom) crossed polarizers. ρ was varied to be (a) 0.87 (L_1 phase), (b) 0.88 (L_1/L_α two-phase), (c) 0.90 (L_1/L_α two-phase), and (d) 0.93 (bluish vesicular phase), respectively.

Surface Tension Measurements. Surface tension measurements were performed on a Processor Tensiometer-K12 (Krüss Company, Germany) using the ring method at 25 °C. The adopted method was called “series measurement” controlled mainly by the tensiometer following the preset parameters. The time interval between each measurement was about 5 min.

Polarized Microscopy Observations. Polarized microscopy observations were carried out on an AXIOSKOP 40/40 FL (ZEISS, Germany) microscope at 25 °C. Three methods were adopted to prepare samples: (a) Two or three drops of aqueous solution to be observed were added on a piece of flat glass and then covered with another piece of flat glass. Observations were carried out immediately after sample loading. (b) A square region was constructed on a piece of flat glass that could store aqueous solutions about 2–3 mm thick. After loading samples into this region, observations were carried out immediately. (c) A special trough of about 4 cm in length, 1.2 cm in width, and 2 mm in height was designed, which could store aqueous solutions for several days without solvent evaporation. The samples were observed both immediately after loading and several days later.

Results and Discussion

Phase Behavior of the TTAOH/LA/H₂O System. Figure 1 gives the water-rich corner of a pseudoternary phase diagram for TTAOH/LA/H₂O at 25 °C. The ranges of c_T and ρ shown are 0–50 $\text{mg} \cdot \text{mL}^{-1}$ and 0.70–1.20, respectively. Samples out of this range are in the extended nearby phase region and are thus cut off for better clarity. On the TTAOH-rich side, an L_1 phase forms whose viscosity increases significantly with increasing ρ (Region I). At the corner of the L_1 phase with higher c_T and ρ , white precipitates form at the bottom (Region II). With increasing ρ , a rich phase behavior is observed at different c_T . In the very dilute L_1 region, macroscopic phase separation occurs with white precipitates at the top when ρ exceeds 0.50 (Region III). This phase separation region extends to the LA-rich side, and the critical c_T value at which the phase separates increases obviously with increasing ρ . So the white precipitates are probably the excess water-insoluble LA that dissociates out of bulk solutions. The bottom phase is either transparent or bluish, depending on the composition of the sample. At medium c_T between 8 and 40 $\text{mg} \cdot \text{mL}^{-1}$, the system reaches an interesting L_1/L_α two-phase region when ρ exceeds 0.87 (Region IV). The L_α phases, which slowly separate out of the bulk solution within

several days after sample preparation, are always at the top and birefringent. However, their appearance and birefringence is different. They are usually transparent and show colorful patterns between crossed polarizers (L_α -1). At the corner with lower c_T and higher ρ , however, they are turbid and show bright strips between crossed polarizers (L_α -2). In occasional cases, we observe a three-phase region with L_α -1 at the top, L_α -2 at medium, and L_1 phase at the bottom, respectively. At higher concentrations, the volume fraction of top L_α phase increases gradually, and finally a single L_α phase forms (Region V). It should be noted that white precipitates were frequently seen within the whole single L_α phase region as well as the L_1/L_α two-phase region with higher c_T . A major reason of the formation of these precipitates should be the existence of excess small counterion OH^- because these regions are located on the TTAOH-rich side. The ionic strength caused by excess OH^- screens the electrostatic interactions between aggregates, just as in the case of salt-containing catanionic systems. At higher ρ , beside the L_1/L_α two-phase region and the L_α phase region is a bluish single phase region that covers nearly one-half of the phase diagram (Region VI). Previous studies on samples with ρ of exactly 1 by freeze-fracture transmission electron microscopy (FF-TEM) revealed the existence of densely packed uni- and multilamellar vesicles.²⁴ For this reason, we call this phase the bluish vesicular phase (L_{av}). But one should keep in mind that other kinds of aggregates such as disk-like micelles and regular hollow icosahedra might also exist when ρ deviated from 1. This is because the current system in this study is similar to that reported by Zemb et al.^{27–30} and also because vesicles and other kinds of aggregates tend to coexist in salt-free catanionic systems.^{20,27} The most pronounced feature of these L_{av} phases is that they are all single phases to the naked eye, and no precipitates form, although recent studies have revealed the hydrophobic chains of surfactants may be in the crystalline state at room temperature.³⁰ This is in sharp contrast with salt-containing catanionic systems where large domains of precipitates were usually observed around the equimolar ratio of cationic and anionic surfactant. This difference is undoubtedly due to the absence or only very small amount of small counterions for the current system. In lower c_T and higher ρ , the L_{av} phase separated into two phases (Region VII).

If we keep c_T fixed and vary ρ (Method a, see Experimental Section) or keep ρ fixed and vary c_T (Method b, see Experimental Section), then sections of the pseudoternary phase

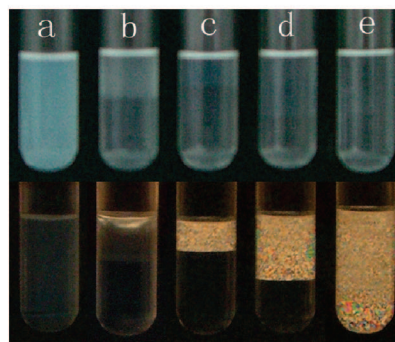
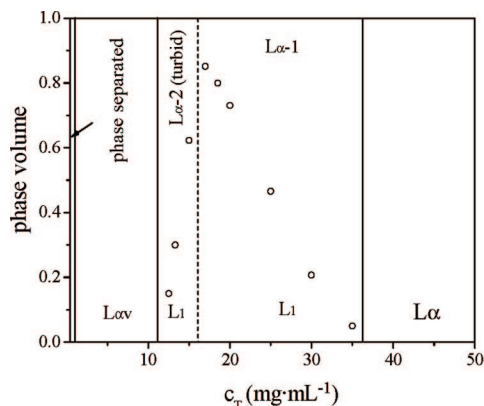


Figure 3. Left: A section of pseudoternary phase diagram with $\rho = 0.91$. The phase volume ratio (○) within the two-phase region was also given. Right: Photos of five typical samples at different regions without (top) and with (bottom) crossed polarizers. c_T was varied to be (a) $10 \text{ mg} \cdot \text{mL}^{-1}$ (bluish vesicular phase), (b) $15 \text{ mg} \cdot \text{mL}^{-1}$ ($L_1/L_{\alpha-2}$ two-phase), (c) $20 \text{ mg} \cdot \text{mL}^{-1}$ ($L_1/L_{\alpha-1}$ two-phase), (d) $30 \text{ mg} \cdot \text{mL}^{-1}$ ($L_1/L_{\alpha-1}$ two-phase), and (e) $40 \text{ mg} \cdot \text{mL}^{-1}$ (single L_{α} phase), respectively.

diagram would be obtained. Two typical examples are given in Figure 2 and Figure 3, respectively. Also included are photos of typical samples within interested phase regions. More photos including those in $L_{\alpha v}$ two-phase region, phase-separated region and $L_1/L_{\alpha-1}/L_{\alpha-2}$ three-phase region can be found in the Supporting Information. For the section with $c_T = 15 \text{ mg} \cdot \text{mL}^{-1}$ but increasing ρ (Figure 2), one observes in turn an L_1 phase, an L_1/L_{α} two-phase, an $L_{\alpha v}$ phase, an $L_{\alpha v}$ two-phase and a phase-separated region. The conductivity decreases significantly on the TTAOH-rich side and then remains almost constant after the equimolar point. The volume fraction of both the upper L_{α} phase within L_1/L_{α} two-phase region and the upper $L_{\alpha v}$ phase within $L_{\alpha v}$ two-phase region increases gradually. For the section with $\rho = 0.91$ but increasing c_T (Figure 3), one observes a phase-separated region at very dilute concentrations. After that, an $L_{\alpha v}$ phase, an L_1/L_{α} two-phase and single L_{α} phase are observed in turn. The L_1/L_{α} two-phase region can be divided into two subregions along the dashed line in Figure 3 according to the appearance of the upper birefringent L_{α} phase, i.e., $L_1/L_{\alpha-2}$ two-phase and $L_1/L_{\alpha-1}$ two-phase. The volume fraction of top L_{α} shrinks gradually at the $L_1/L_{\alpha-2}$ two-phase region, passes through a minimum and then increases gradually up to unity at the $L_1/L_{\alpha-1}$ two-phase region.

Surface Tension Measurements. Since most of the solid surfaces in aqueous solutions are negatively charged, cationic surfactants adsorb preferentially onto these surfaces.⁴ This makes it difficult to accurately determine the surface tension of cationic and anionic surfactant mixtures. To minimize this disadvantage, the dishes were usually pretreated by multirinsing or long-time soakage with the solution measured in previous studies of salt-containing catanionic systems.^{4,5,9} In the current study, we adopt the series measurement method, and two typical results are shown in Figure 4. Because at higher ρ phase separation occurs for TTAOH/LA/H₂O system, measurements were only performed for samples at $\rho \leq 0.50$. The measurements gave well-resolved data with critical micellar concentration (cmc) equal to or slightly higher than $0.1 \text{ mmol} \cdot \text{L}^{-1}$. This is consistent with the values obtained for salt-containing catanionic systems but in contrast with those obtained for single-chain cationic and anionic surfactants including TTABr (cmc: $3.7 \text{ mmol} \cdot \text{L}^{-1}$),³³ TTAOH (cmc: $1.8 \text{ mmol} \cdot \text{L}^{-1}$ from surface tension measurement and $3.6 \text{ mmol} \cdot \text{L}^{-1}$ from conductivity measurement),^{24,31} and SDS (cmc: $8.1 \text{ mmol} \cdot \text{L}^{-1}$).³⁴ The high effectiveness of lowering surface tension for catanionic systems can be explained by an effective reduction of the area of their hydrophilic headgroups after ion-pairing between cationic and anionic surfactants,

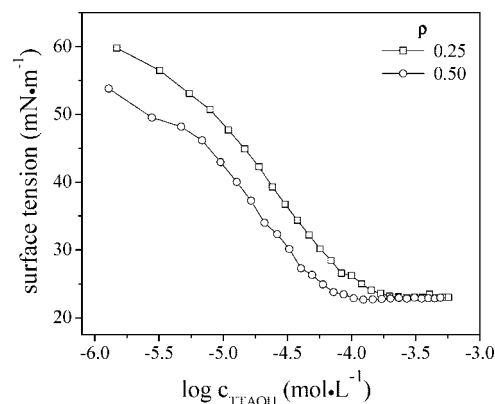


Figure 4. Semilog plot of surface tension versus concentration of TTAOH for two series of samples with different ρ as indicated in the inset.

resulting in more densely packing at the air/water interface compared to single cationic or anionic surfactants.

Rheological Properties: A General View. Rheological study can provide more detailed information about aggregate transition compared to macroscopic phase behavior study. Within the same phase region (such as the L_1 phase region), the type and dimension of the aggregates may be different, which will be reflected in their rheological properties. The rheological properties of the TTAOH/LA/H₂O system are found to be dominated by several factors. In our current study, we focus our attention on influences of ρ , c_T , and temperature. Mainly three regions exhibiting different rheological properties are our current interest: the shear thickening rod-like micelles, the viscoelastic worm-like micelles, and the gel-like densely packed vesicles. The rheological properties of the interesting L_1/L_{α} two-phase region will also be discussed both as a whole before phase separation and on each individual phase. In the following sections, we would like to discuss the influence of ρ at fixed c_T first and then give a detailed discussion about the influence of c_T and temperature within each region of interest.

Influence of ρ at Constant c_T . With increasing ρ , more catanionic ion-pairs form, and the critical packing parameter of surfactants³⁵ changes continuously. This will induce a subsequent aggregate transition from globular micelles to rod-like and worm-like micelles and finally to flat or closed bilayer. In some cases, different aggregates may coexist in the same sample, leading to the formation of multiphase regions. This is indeed the knowledge we have learned from phase behavior study. As a macroscopic reflection of the microscopic aggregate

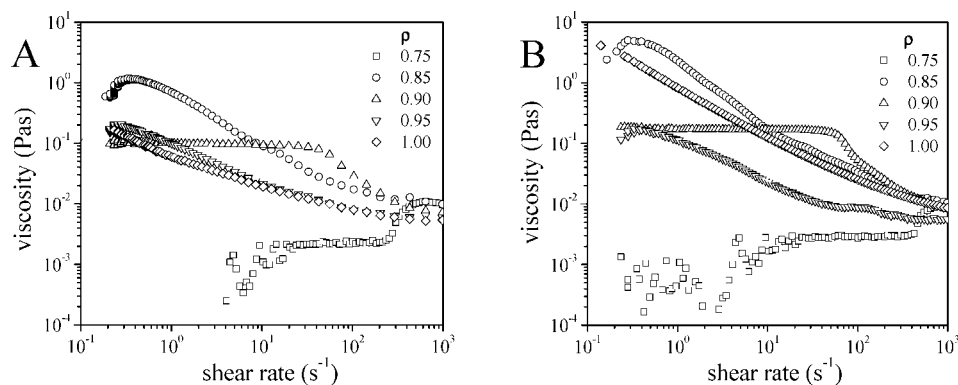


Figure 5. Shear viscosity as a function of shear rate at different ρ as indicated in the inset for two series of samples with c_T at 15 mg·mL⁻¹ (A) and 25 mg·mL⁻¹ (B), respectively. The samples with $\rho = 0.90$ are already within the L_1/L_{α} two-phase region. Measurements on them were carried out before phase separation.

transition, the rheological properties of the TTAOH/LA/H₂O system at fixed c_T change significantly with increasing ρ . Figure 5A,B shows the viscosity as a function of shear rate obtained from steady shear experiments for two series of samples with c_T at 15 mg·L⁻¹ and 25 mg·L⁻¹, respectively. The evolution of the curves with ρ is similar, although some differences have also been observed. For better clarity, only selected curves are shown, and the detailed rheological properties within each region will be discussed in more details in the following sections. At low ρ , the sample is low viscous and shows Newton fluid character. With increasing ρ , the viscosity increases gradually, and a shear thickening behavior is observed at $\rho > 0.70$ with critical shear rate on the order of several hundred s⁻¹. The shear thickening behavior is strongest around $\rho = 0.75$ and then weakens. When ρ exceeds 0.81, the system enters a highly viscous worm-like micelle region. The worm-like micelles exhibit a viscosity plateau called zero shear viscosity (η_0) and a critical shear rate (γ_c) at which shear thinning behavior is observed. When ρ increases gradually from the boundary of the shear thickening region, η_0 increases significantly at first and reaches a maximum at about $\rho = 0.825$. Then a continuous decrease of η_0 is observed with an opposite variation of γ_c to higher values. This type of curve extends into the L_1/L_{α} two-phase region, as can be seen for the sample with $\rho = 0.90$, when measurements are carried out before phase separation. For samples with highest η_0 , γ_c is usually very low (<0.1 s⁻¹) and the sample usually shows a pseudoshear thickening behavior at low shear rates. This is probably due to the longer time the sample requires to reach steady state at low shear rates and to recover by themselves once disturbed by external shear, including loading the sample into the coaxial cylinder. The $L_{\alpha v}$ phase at $\rho = 1.00$ shows shear thinning behavior, which is consistent with previous results of densely packed vesicles formed both in TTAOH/LA/H₂O and other similar systems.^{14–24} Samples with 25 mg·mL⁻¹ have yield stress values and can trap small air bubbles. When LA is in excess, their rheological properties vary only slightly and even superpose with each other (data not shown). Samples at 15 mg·mL⁻¹ lose yield stress values, and measurements are not carried out on the LA-rich side because of phase separation. The rheological properties of the $L_{\alpha v}$ phases on the TTAOH-rich side ($\rho = 0.95$) seem to be the transition region between worm-like micelles and densely packed vesicle phases.

When measurements were carried out on samples with higher concentrations (for example, $c_T = 30$ mg·mL⁻¹, see Supporting Information), evolution of the rheological curves is also the same. But variations of the boundaries between each region

become more obvious. The influence of c_T and temperature will be discussed in more details within each region in the following sections.

Shear Thickening Region. Shear thickening behavior has already been observed in several other surfactant systems,^{36–38} and the mechanism has been discussed and known for many years.³⁹ Surfactant systems exhibiting shear thickening behavior typically contain rod-like micelles a few tens of nanometers long, and their separation is somewhat larger. These micelles undergo free Brownian motions at equilibrium state or under slow shear rates. When the applied shear rate is above a critical value, however, they tend to align in the shear flow. As a result, colloids and rearrangements occur, and larger aggregates are formed. Together with shear thickening behavior, some of the parameters of the solutions will also change drastically, such as a sudden increase of flow birefringence and a sudden decrease of the angle of extinction.³⁹ Figure 6A,B shows the influence of concentration and temperature on the shear thickening behavior of a TTAOH/LA/H₂O system, respectively. An increase of concentration induces a corresponding increase of viscosity with weakened shear thickening behavior (Figure 6A). At the highest concentration of 60 mg·mL⁻¹, the shear thickening behavior disappears completely, and a shear thinning behavior is observed. This can be explained by the growth of the rod-like micelles and the increase of their number density at higher surfactant concentrations. The elongated rod-like micelles would then exceed their separation and even form worm-like micelles, accounting for the increase of viscosity and loss of shear thickening behavior. The shear thickening behavior also weakens at higher temperatures, as can be seen from Figure 6B. The critical shear rate at which shear thickening occurs moved to higher values and the viscosity of the samples decreases gradually. It can be inferred shorter micelles form with increasing temperatures because micelle growth will be greatly suppressed at higher temperatures. Thus colloids and rearrangements become more and more difficult for the continuously shortened rod-like micelles.

Rheological Properties of Worm-like Micelles. Adding salt into cationic surfactant aqueous solutions usually induces an obvious micelle growth, especially when the added salt can strongly bind to the headgroup of cationic surfactant.^{40–52} Typical binding salt used to induce micelle growth is sodium salicylate.^{42,44,47–52} Worm-like micelles have also been observed in aqueous solutions of anionic surfactants,^{53–55} nonionic surfactants,^{56,57} and catanionic surfactant mixtures.^{6–8,12,13} The quantitative features of these worm-like micellar systems vary from one system to the other. However, they share in common some

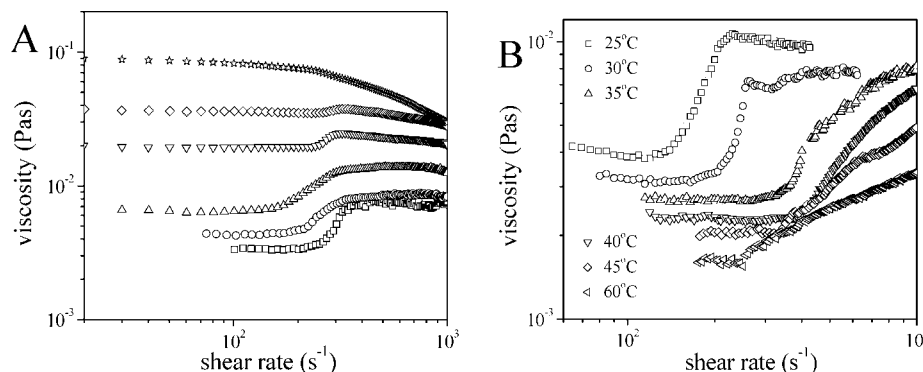


Figure 6. Change of shear thickening behavior as a function of concentration (A) and temperature (B). $\rho = 0.75$. Concentration in graph A is 10 (□), 20 (○), 30 (Δ), 40 (▽), 50 (◇) and 60 (☆) mg·mL⁻¹. The sample used in the temperature test has a concentration of 15 mg·mL⁻¹.

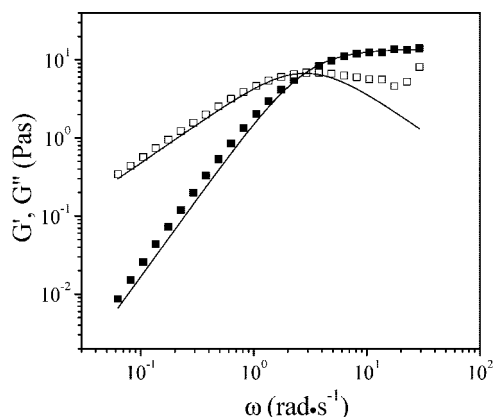


Figure 7. Elastic modulus G' (solid symbols) and viscous modulus G'' (open symbols) as a function of angular frequency ω for a sample with $c_T = 30$ mg·mL⁻¹ and $\rho = 0.825$. The solid lines are fits according to the Maxwell model.

elementary characteristics. They have a plateau of viscosity, called zero shear viscosity η_0 , at low shear rates and show shear thinning behavior above a critical shear rate γ_c in steady shear flow. Usually they are highly viscous but also have elastic properties due to the formation of a transient network.

The viscoelastic behavior of worm-like micelles is known to be reminiscent of that of “living” polymers and can be described by a model developed by Cates and co-workers.^{58–61} This model involves two relevant time scales: the reptation time τ_{rep} and the breaking time τ_{break} . If $\tau_{break} \ll \tau_{rep}$, chain breakage and recombination will both occur often. The stress relaxation is then characterized by a new intermediate time scale τ_R . In low

frequencies of oscillatory measurements, the behavior of the system can be described by the Maxwell model, where G' increases monotonously with increasing ω and approaches G_0 at high frequency, while G'' increases at first, reaches a maximum, and then decreases continuously. Figure 7 gives a typical result obtained from oscillatory shear measurement for worm-like micellar solutions formed in a TTAOH/LA/H₂O system. One can see that the fit of G' and G'' according to the Maxwell model is satisfactory. The high-frequency plateau modulus G_0 and relaxation time τ_R can be calculated to be 13.5 Pa and 0.35 s, respectively, from the values of ω^* and G^* at the intersection. At high frequencies, G'' deviates from the Maxwell model as a result of the appearance of a new relaxation mode called the Rose relaxation mode.⁶²

The elementary characteristics of worm-like micelles including η_0 , γ_c , G_0 and τ_R are strongly influenced by solution parameters such as ρ , c_T , and temperature. Figure 8A,B shows the results of shear viscosity as a function of shear rate and complex viscosity as a function of angular frequency for samples with $c_T = 15$ mg·mL⁻¹ and varying ρ from 0.80 to 0.88, respectively. The sample with lowest ρ of 0.80 only contains rod-like micelles and shows a shear thickening behavior. With increase in ρ , worm-like micelles with very high η_0 and low γ_c form within a narrow range of $0.82 \leq \rho \leq 0.865$. These solutions show pseudoshear thickening regions at low shear rates, as has been mentioned in the previous section. In steady shear flow where shear rate is increased gradually from very low value to high value in limited time, the fluid with high viscosity and long recovery time may not reach steady state, especially in low shear rates, accounting for the appearance of the pseudoshear thickening region in the current case. Fortu-

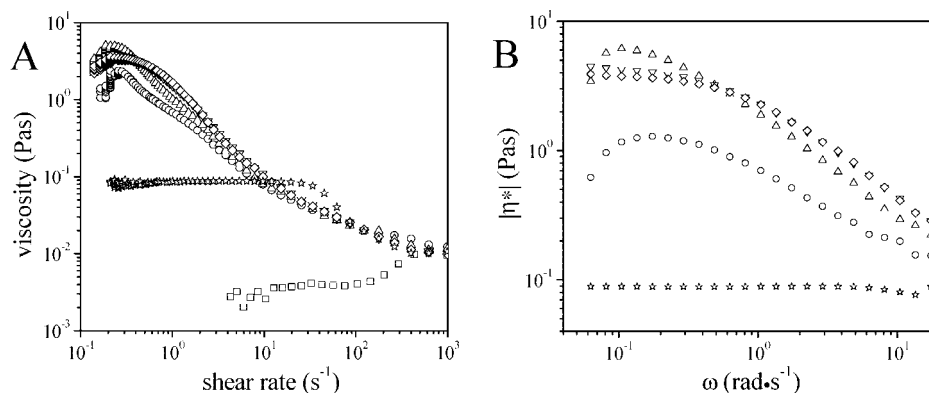


Figure 8. Shear viscosity as a function of shear rate (A) and complex viscosity as a function of angular frequency (B) for samples with $c_T = 15$ mg·mL⁻¹ and ρ values of 0.80 (□), 0.82 (○), 0.835 (Δ), 0.85 (▽), 0.865 (◇) and 0.88 (☆). The complex viscosity of the sample with $\rho = 0.80$ was not available because of lack of a linear viscoelastic region in the stress sweep.

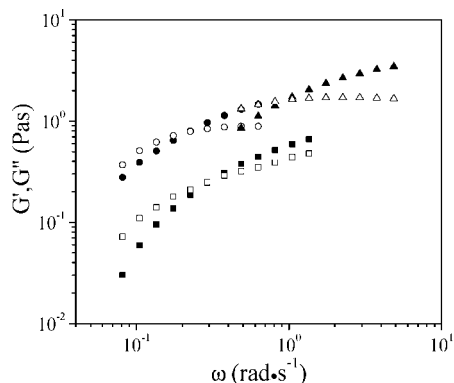


Figure 9. Elastic modulus G' (solid symbols) and viscous modulus G'' (open symbols) as a function of ω for three samples with $c_T = 15 \text{ mg} \cdot \text{mL}^{-1}$ and different ρ values of 0.82 (square), 0.835 (circle), and 0.85 (triangle).

nately, in practice it is found that the relationship between shear viscosity η and shear rate $\dot{\gamma}$ in steady shear measurement resembles that between η' ($= G''/\omega$) and angular frequency ω in oscillatory measurement, where data were recorded usually in longer time scales. While $\eta' \approx \eta^*$ at low angular frequencies, this shortcoming can be eliminated more or less by observing the relationship between complex viscosity η^* and angular frequency ω in oscillatory measurements (Figure 8B). Interestingly, the shear thickening region can be still seen for the two samples with ρ to be 0.82 and 0.835. The reason is currently not very clear, but we would still assign this phenomenon to be an artifact caused by the shear history, including loading the samples into the coaxial cylinder. Since all the experiments were done under similar conditions, Figure 8B also indicates the recovery time for these two samples is longer than others. This is also consistent with their longer relaxation time τ_R seen from Figure 9. The result of the sample with $\rho = 0.865$ is very similar to that of $\rho = 0.85$, and the two curves are nearly overlapped, so we do not show it in Figure 9. When ρ exceeds 0.865, η_0 decreased rapidly with a gradual increase of γ_c , as can be seen clearly from the sample with highest ρ of 0.88.

Figure 10A,B shows the results of shear viscosity as a function of shear rate and complex viscosity as a function of angular frequency for samples with $\rho = 0.825$ and varying c_T . Again the shear thickening behavior of the sample with c_T of $20 \text{ mg} \cdot \text{mL}^{-1}$ can be ascertained to be a pseudo phenomenon by observing the relationship between η^* and ω in oscillatory measurements. With increasing c_T , η_0 increases at first, reaches a maximum at $20 \text{ mg} \cdot \text{mL}^{-1}$ and then decreases continuously. The first increase of η_0 can be ascribed to an increase in entanglement points of worm-like micelles. The subsequent decrease of η_0 with further increasing c_T has also been observed in many other worm-like micellar systems and has been argued for years. Now it is believed this phenomenon is due to an aggregate transition from entangled worm-like micelles to branched worm-like micelles, which have been directly observed by cryogenic TEM (cryo-TEM).^{57,63,64} The junctions of branched worm-like micelles are not fixed and can slide along the backbones, providing another mode for strain relaxation. This can explain the lower η_0 obtained from steady shear measurement (Figure 10) and also accounts for the lower relaxation time τ_R that can be seen from results of oscillatory measurements (Figure 11).

One of the biggest differences between worm-like micelles ("living" polymers) and "dead" polymers is that worm-like micelles are always in equilibrium with surfactant unimers and

undergo fast mass exchange. So their behavior is well expected to depend greatly on temperature. Figure 12A shows the rheological properties of a worm-like micellar solution as a function of temperature. One can see η_0 decreases continuously and γ_c becomes larger with increasing temperature. At the highest temperature of 55°C , a Newton behavior is observed within the whole measured shear rates. Oscillatory measurements reveal the elastic property of the sample losses significantly at higher temperatures. In fact, G'' is higher than G' over the whole measured ω range once the temperature exceeds 30°C .

Theory and experiments suggest that the micellar contour length decays exponentially with increasing temperature. Concomitantly, key rheological parameters such as η_0 and τ_R also decay exponentially, as described by Arrhenius relationships:

$$\eta_0 = G_0 A e^{E_a/RT} \quad (1)$$

$$\tau_R = A e^{E_a/RT} \quad (2)$$

where E_a is the flow activation energy, T is the absolute temperature, R is the gas constant, and A is a pre-exponential factor. According to eqs 1 and 2, semilog plots of η_0 and τ_R versus $1/T$ should be a straight line, and from its slope E_a can be calculated. Such a plot of η_0 is included in Figure 12B. The fit of τ_R can not be obtained because of the loss of viscoelastic property of the sample at higher temperatures. To our disappointment, the Arrhenius fit of η_0 separates into two parts, yielding an activation energy of $264 \text{ kJ} \cdot \text{mol}^{-1}$ at low temperature range and $103 \text{ kJ} \cdot \text{mol}^{-1}$ at higher temperatures. An average value of $183.5 \text{ kJ} \cdot \text{mol}^{-1}$ is obtained, which falls into the normal region of E_a ($70\text{--}300 \text{ kJ} \cdot \text{mol}^{-1}$) reported for various worm-like micellar solutions. The reason for this nonlinear fit is currently not very clear. However, it is probably caused by the high chain melting temperature of LA, which is about 44°C ($1000/T = 3.15$). Below and above this temperature, the micellar contour length may vary in a different way, accounting for the appearance of an inflection. Similar phenomenon has also been observed in a CTABr system, where the Arrhenius fit of η_0 differs below and above the Krafft point of CTABr.^{43,44} Currently, the possibility of coexistence of other kind of aggregates such as closed or flat bilayers can not be excluded since this sample is near the phase boundary of the L_1/L_α two-phase region.

Rheological Properties of L_{av} Phases. The rheological property of L_{av} phases differs before and after the equimolar ratio. At the equimolar ratio and LA-rich side ($\rho \geq 1$), the L_{av} phase has a yield stress value and can trap small air bubbles even when c_T is as low as $20 \text{ mg} \cdot \text{mL}^{-1}$. They show a shear thinning behavior in steady shear measurements (Figure 13) and a gel-like behavior in oscillatory measurements (Figure 14). The characteristics of their rheological properties are typical of densely packed vesicles, as have been described by Hoffmann et al. and by us previously in many similar systems.^{14–26} At $\rho \geq 1$, the system lacks any small counterions because OH^- reacts with equimolar H^+ to form water and the excess water insoluble LA does not dissociate. So the ionic strength of the system is very low, and the electrostatic interactions between aggregates are not shielded. The bilayers thus repel each other and the vesicles can not pass each other in shear flow without becoming deformed, accounting for the yield stress value and gel-like behavior.³⁹ It should also be noted that the rheological properties vary only slightly for samples with the same c_T . In fact, the curves of the samples with ρ to be 1.00, 1.05, 1.10, 1.05, and 1.20 at fixed c_T of $25 \text{ mg} \cdot \text{mL}^{-1}$ or $30 \text{ mg} \cdot \text{mL}^{-1}$ nearly

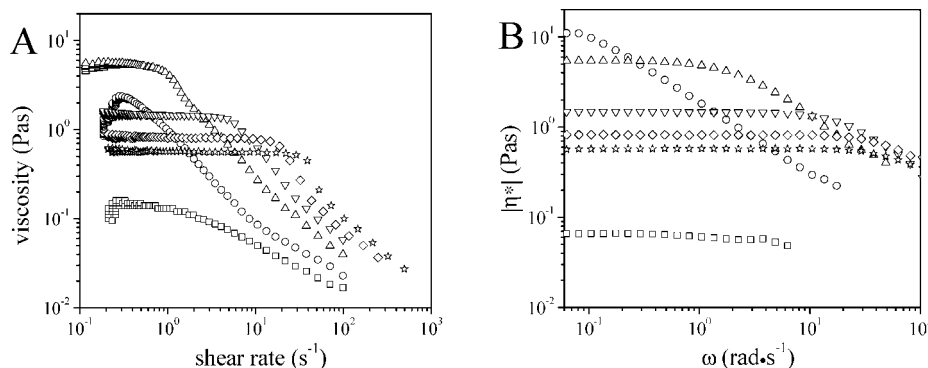


Figure 10. Shear viscosity as a function of shear rate (A) and complex viscosity as a function of angular frequency (B) for samples with $\rho = 0.825$ at concentration of 10 (□), 20 (○), 30 (Δ), 40 (▽), 50 (◇) and 60 (☆) mg·mL⁻¹.

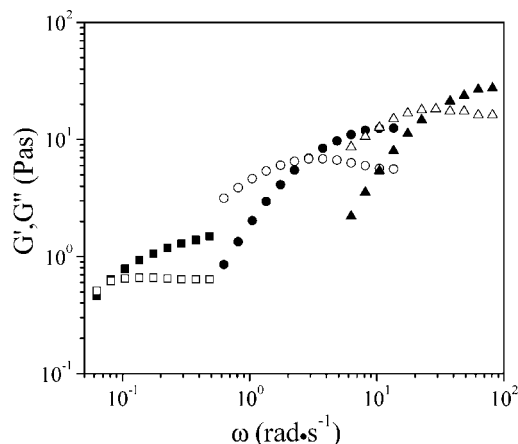


Figure 11. Elastic modulus G' (solid symbols) and viscous modulus G'' (open symbols) as a function of ω for three samples with $\rho = 0.825$ and different concentrations of 20 (square), 30 (circle), and 40 mg·mL⁻¹ (triangle).

superpose with each other (data not shown). On the TTAOH-rich side ($\rho < 1$), the characteristics of the $L_{\alpha v}$ phase are between those of worm-like micelles and densely packed vesicles. So they seem to be a transition region from micelles to vesicles.

The rheological properties of densely packed vesicles are found to be changed only slightly against temperature rise. At higher temperatures, both shear stress and viscosity show some degree of decrease (Figure 15 A,B). This decrease is, however, much gentler than that of micellar solutions. More importantly, oscillatory measurement reveals that the sample is still highly elastic and shows a gel-like behavior even when the temperature is as high as 60 °C (data not shown). In fact, the viscoelastic behavior of the sample at 60 °C is almost the same as that at 25 °C. This is in sharp contrast with the worm-like micelles whose viscosity decreases greatly with increasing temperature. This difference originates from the different characteristic of the two systems. The elasticity of worm-like micelles is due to the formation of a transient network, and the modulus is given by entropic forces.³⁹ However, the densely packed vesicles are stabilized by energy, i.e., by unscreened electrostatic interaction.³⁹ Temperature rise will cause significant change of entropy but only little change of energy. There is another factor that may also account for this question. The chain melting temperature of LA is about 44 °C, so the input energy by temperature rise may be consumed upon melting the chains of LA below 44 °C rather than induce aggregate transition. Of course, aggregate transition between vesicles and other kind of aggregates during temperature variation can be well expected to occur, as has been clarified by Zemb et al. in a similar

system.^{29,30} However the dimensions of these aggregates are usually of the same order of magnitude and thus can not induce obvious change in the rheological properties.^{29,30}

Properties of the L_1/L_α Two-Phase Region. Aqueous two-phase regions are frequently seen both in salt-containing and salt-free catanionic systems. The microstructures in each region may differ with each other in different systems, but the driving force is usually the same, i.e., the difference of density between coexisting aggregates. In the current case, the L_1/L_α two-phase region locates between worm-like micelles and bluish vesicular phases. It can be well inferred within this region that worm-like micelles, which are rich in TTAOH, and flat or closed bilayers, which are rich in LA, coexist. Because the density of bilayers is lower than that of micelles, they separate out of the bulk solutions slowly and form the upper L_α phase. The appearance of the upper L_α phase will depend on parameters of these bilayers such as the dimension of each individual bilayer, the distance of neighboring bilayers, and the arrangement mode of the bilayer (closed or flat). This conclusion is confirmed by the results obtained by Hoffmann et al. for many other similar systems where bilayers of different types were clearly seen by FF-TEM observations.^{14,18–23,39}

The rheological properties of the L_1/L_α two-phase region before phase separation resemble those of worm-like micelles, as can be seen from Figure 5. To see the individual rheological properties of the upper L_α phase and bottom L_1 phase, we also combine the L_1/L_α two-phase region at fixed c_T of 25 mg·mL⁻¹. The final ρ is calculated to be around 0.91. After phase equilibrium, the upper L_α phase and bottom L_1 phase were collected separately. Their rheological properties obtained from steady shear measurements are shown in Figure 16. It can be seen that the rheological property of the L_1 phase is typical of worm-like micelles, while, for the upper L_α phase, a shear thinning behavior is observed until a constant viscosity is reached at higher shear rates. This shear thinning behavior of L_α phase can be ascribed to the alignment of bilayers along shear flow. When the alignment is completed, the viscosity does not decrease, and a constant value is reached.

The L_α phases both within the L_1/L_α two-phase region and the L_α /precipitate region are birefringent, which can be seen with the help of crossed polarizers. It also can be better understood under a polarized microscope. The method adopted to prepare samples is found to have an obvious influence on the observed textures. No obvious birefringence can be observed for very thin samples prepared between two pieces of flat glass (Method a, see Experimental Section). Samples 2–3 mm thick prepared within the square region of flat glass (Method b, see Experimental Section), however, always show obvious bire-

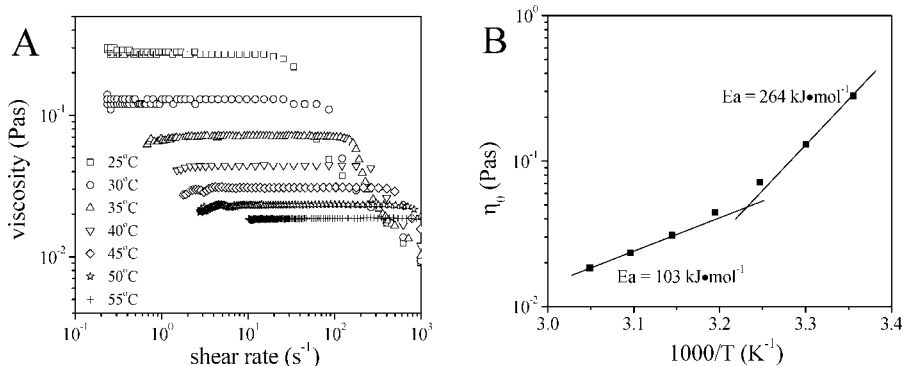


Figure 12. (A) Shear viscosity as a function of shear rate at different temperatures as indicated in the inset for a sample with $c_T = 30 \text{ mg} \cdot \text{mL}^{-1}$ and $\rho = 0.85$. (B) Arrhenius fit of zero-shear viscosity η_0 .

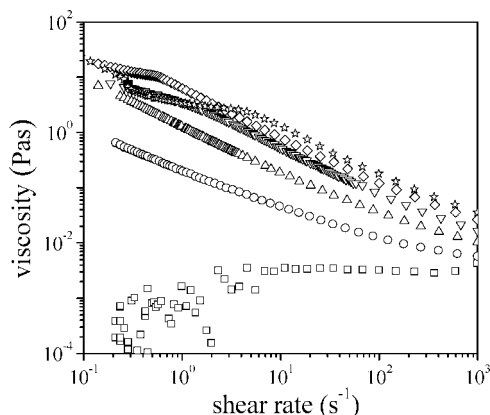


Figure 13. Shear viscosity as a function of shear rate for samples with ρ of 1.00 and c_T values of 10 (\square), 20 (\circ), 30 (Δ), 40 (∇), 50 (\diamond) and 60 (\star) $\text{mg} \cdot \text{mL}^{-1}$.

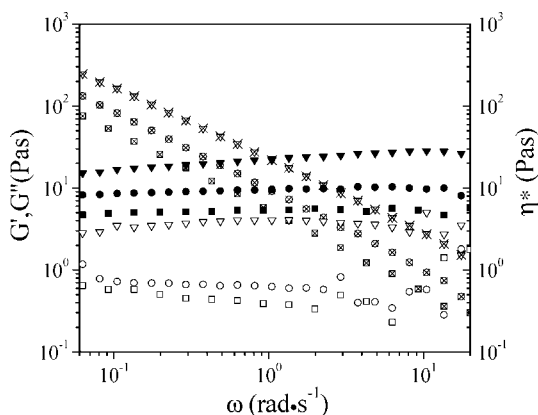


Figure 14. Elastic modulus G' (solid symbols), viscous modulus G'' (open symbols), and complex viscosity η^* (open symbols with internal crosses) as a function of ω for typical $L_{\alpha v}$ phases at $\rho \geq 1.00$. Squares: $\rho = 1.00$, $c_T = 25 \text{ mg} \cdot \text{mL}^{-1}$; circles: $\rho = 1.10$, $c_T = 30 \text{ mg} \cdot \text{mL}^{-1}$; triangles: $\rho = 1.363$, $c_T = 50 \text{ mg} \cdot \text{mL}^{-1}$.

fringence, and two typical photos are given in Figure 17 (more images can be found in the Supporting Information). The detailed birefringence may be different from one sample to another and even in different regions of the same sample. The difference may come from different parameters of bilayers and also from external disturbance during sample loading, say, an external shear force when dropping solutions onto the glass.

To see the influence of shear on the birefringence, a special trough was designed, which can store samples for longer time without solvent evaporation (Method c, see Experimental Section). The birefringence of two L_{α} phases with different

compositions were examined both immediately after loading and four days later. It is found that the birefringence does change with time and becomes stronger. At the same time, new structures appear, which look like tapers and show crosses under illumination of light (Figure 18; for more images, see Supporting Information). The evolution of the birefringence with time is probably a result of the recovery of bilayers with time after external shear is removed. It should be noted that another important factor may also account for this phenomenon, especially for the formation of taper-like structures, that is, the alignment of surfactants or phases along the glass surface. Currently we are unable to ascertain that this process does occur. But the alignment-induced phenomena have already been observed in other surfactant systems. For example, Hoffmann pointed out that the Schlieren texture of a freshly filled thin cuvette disappears with time because of the alignment of the phase if it is a nematic disk phase.³⁹ The formation of giant vesicles from large unilamellar vesicles on or close to glass substrates has also been observed for many fatty acid/soap systems.⁶⁵

Aggregate Transition in Catanionic Systems. Before discussing aggregate transition in catanionic system, we would like to mention the critical packing parameter p of surfactant,³⁵ which has been known for many years:

$$p = V/la_0 \quad (3)$$

where V and l are the volume and length of hydrophobic chain, respectively, and a_0 is the area of hydrophilic headgroup. By simple mathematical transform, we can obtain equation 4:

$$p = (V/l)/a_0 = a_s/a_0 \quad (4)$$

where a_s is the area of cross section of the hydrophobic chain. Equation 4 is easier understood than equation 3, and is most useful for single-chain ionic surfactants. The value of p has been acting as a guide for people to speculate what kind of aggregate will form in aqueous solutions for a given surfactant, as shown in Table 1.

For single chain cationic or anionic surfactants, a_s is almost constant and is nearly independent of solution parameters. It is also independent of hydrophobic chain length, although there are also different opinions. However, a_0 is influenced significantly by the ionic strength of the solution. In single-component aqueous solutions of cationic and anionic surfactants such as TTABr and SL (Scheme 1), a_0 is generally much larger than a_s , and the molecular shape can be viewed as a taper. Both of them tend to form small globular micelles. In equimolar mixtures of SL and TTABr, a_s doubles, but a_0 decreases significantly as a result of the formation of catanionic ion-pairs. The molecular

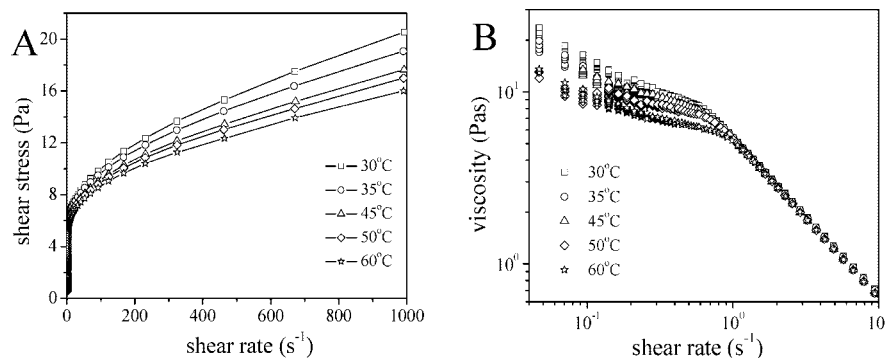


Figure 15. Plot of shear stress (A) and viscosity (B) as a function of shear rate at different temperatures on a sample with $c_T = 50 \text{ mg} \cdot \text{mL}^{-1}$ and $\rho = 1.00$.

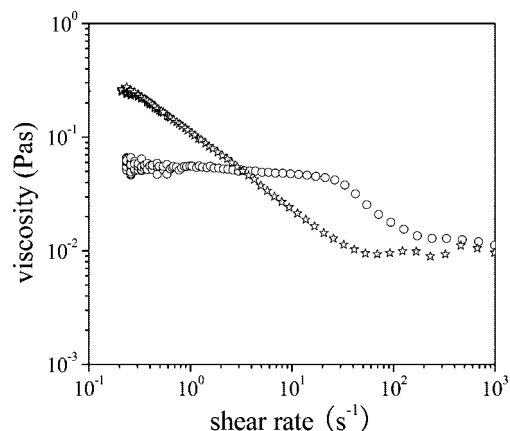


Figure 16. Shear viscosity as a function of shear rate for the bottom L_1 phase (○) and upper L_α phase (☆) within the L_1/L_α two-phase region. $c_T = 25 \text{ mg} \cdot \text{mL}^{-1}$. ρ is calculated to be around 0.91.

shape of a typical catanionic ion-pair TTAL can be viewed as a column. This will induce the formation of closed or flat bilayers. When the mixing molar ratio of SL to TTABr varies from 0 to 1 and higher, the molecular shape will adopt an average value between a taper and a column, varying from a taper to a column and then to a taper again. This induces a colorful aggregate transition and accounts for a rich phase behavior observed in catanionic systems. In some cases different kinds of aggregates may coexist in one sample. Because the composition of cationic and anionic surfactant may be different in different kinds of aggregates, a difference of density may be induced, and the sample will subsequently separate into two or more phases.

The formation of catanionic ion-pairs will lead to other effects that should not be neglected. The electrostatic repulsion between individuals is lost after ion-pairing. Of course the aggregates may still carry some charges even in equimolar ratio originating from the dissociation of ion-pairs. However these charges are shielded by the excess salt or, more precisely, the small counterions. What's more, the molecular weight of the ion-pair is higher than the individual one. These factors will account for the formation of the precipitates that have been frequently seen in conventional salt-containing catanionic systems, especially around equimolar ratio. The domain of precipitates in the phase diagram of catanionic systems differs from one system to another. Precipitate formation can also be suppressed more or less by altering the headgroups or chain symmetry of cationic and anionic surfactants.²⁻⁹

Comparison between a Salt-Free Catanionic System and a Salt-Containing One. The most pronounced feature of a salt-free catanionic system is the absence of excess salt because OH^-

reacts with H^+ to form water. The ionic strength is thus low, and the electrostatic interactions between aggregates are thus unscreened. This point has already been clarified in the first two parts of this paper and accounts for the formation of the wide-range L_{av} phase in Figure 1. On the TTAOH-rich side, where OH^- is in excess, the increase of ρ at fixed c_T will result in two conflict effects. The amount of excess OH^- decreases with increasing ρ . Thus the electrostatic interactions between aggregates will be less screened, making the system more stable. However, the surface charge density of aggregates will decrease with increasing ρ because more cationic surfactant TTAOH will react with LA. This will cause a decrease of electrostatic repulsion between aggregates and make the system unstable. Increasing c_T at fixed ρ may not alter the surface charge density of aggregate, but does increase the number density of aggregates and ionic strength. The final observed precipitate formation within the L_α phase region and corners of L_1 as well as the L_1/L_α two-phase region should be a synthetic result of these factors mentioned above.

It should be emphasized there are other differences between the current system and salt-containing ones that should not be neglected. Take TTABr/SL/ H_2O as a contrast, and let us see what will happen if we replace the counterions Br^- and Na^+ with OH^- and H^+ , respectively. One will easily find that TTAOH has a molecular shape similar with that of TTABr (Scheme 1) and tends to form globular micelles in aqueous solution. The catanionic ion-pairs formed by TTAOH and LA are exactly the same with those formed by TTABr and SL. However, the properties of LA change significantly compared to its sodium form SL. Two important points should be recognized: (a) LA has a chain melting point of about 44 °C, well above room temperature, and (b) LA is difficult to dissociate and almost insoluble in water. Generally speaking, the chain melting temperature or Krafft point of most selected cationic and anionic surfactants studied are well below room temperature. For example, the chain melting temperature or Krafft point of SL is only about 20 °C. Although the high chain melting temperature of LA alone can not induce precipitate formation in the current system, as can be seen from the single phase formation in the LA-rich side (Figure 1), it may also contribute more or less to the precipitate formation. This is confirmed by the fact that the L_{av} phase easily forms crystals when the temperature is below 15 °C. Our further study also provides additional proofs. When LA is replaced by longer chain fatty acids including MA, palmitic acid (PA) and stearic acid (SA), precipitates are easier found at 25 °C in the sequence $\text{SA} > \text{PA} > \text{MA}$.⁶⁶ This sequence is consistent with that of their chain melting temperature. Besides phase behavior, the higher chain melting temperature of LA compared with that of

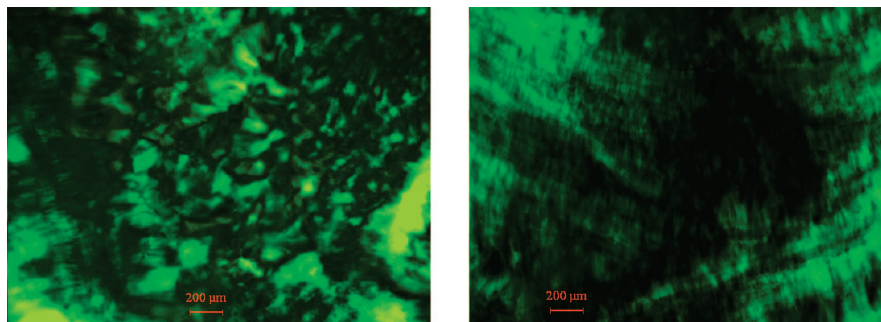


Figure 17. Typical polarized images of the upper L_α phase with $\rho = 0.93$, $c_T = 25 \text{ mg} \cdot \text{mL}^{-1}$ (left), and the L_α phase with $\rho = 0.91$, $c_T = 40 \text{ mg} \cdot \text{mL}^{-1}$ (right).

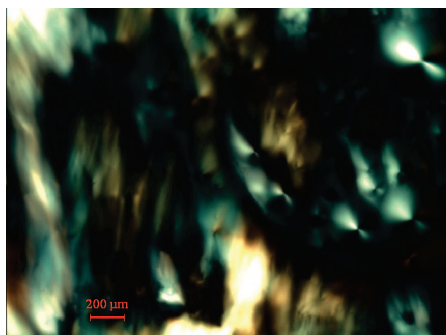
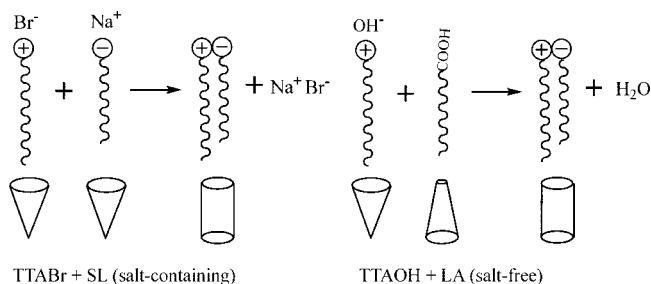


Figure 18. A typical polarized image recorded 4 days after sample preparation. $\rho = 0.92$, $c_T = 37.5 \text{ mg} \cdot \text{mL}^{-1}$.

TABLE 1: Relationship between p and the Type of Aggregate Formed by Surfactants

| value of p | type of aggregates |
|--------------------|-------------------------|
| $p \leq 1/3$ | globular micelles |
| $1/3 < p \leq 1/2$ | rod-like micelles |
| $1/2 < p \leq 1$ | closed or flat bilayers |
| $p > 1$ | reverse structures |

SCHEME 1



conventional anionic surfactants may also account for many other unique phenomena, such as the nonlinear fit of η_0 to Arrhenius equations and the considerable temperature resistance of vesicles, which have been discussed in detail in previous sections.

As for the second feature, LA acts as a long-chain alcohol and can be viewed as a cosurfactant rather than surfactant in the LA-rich side where the acid–base neutralization reaction does not work. Because LA is difficult to dissociate, the conductivity and ionic strength almost remained the same, accounting for the similarity of phase behavior and rheological properties of the $L_{\alpha v}$ phases in the LA-rich side. Also because of its poor hydrophilicity, a_s is well expected to be larger than a_0 , and the molecular shape of LA is like a sectional taper (Scheme 1). This molecular feature makes it possible to construct reverse structures such as interesting reverse vesicles

in organic solvents by carefully monitoring the ratio between LA and TTAOH.^{67,68}

Conclusion

To conclude, salt-free catanionic system TTAOH/LA/H₂O exhibits a rich phase behavior with variation of mixing molar ratio and total surfactant concentration. Correspondingly, the rheological property of the system changes significantly. This should be a result of aggregate transition between different types driven by a continuous change of the average critical packing parameter of the mixed surfactants. The rod-like micelles with suitable size and number density show shear thickening behavior. For the long, flexible worm-like micelles, viscoelastic properties are observed due to the formation of a transient network, and the samples show Maxwell fluid character. The densely packed vesicles, which are stabilized by unscreened electrostatic repulsions, show a gel-like behavior due to the formation of a real network. It is found that micelle growth will be greatly suppressed at higher temperatures, as can be seen from both the rod-like micelles and worm-like ones. However, the densely packed vesicles show a considerable high resistance against temperature rise. This may find applications where the environmental temperature is above room temperature. In samples where different types of aggregates coexist, phase separation will occur if the density is different. The top birefringent L_α phase, as proved by polarized microscope, contains closed or flat bilayers, and its rheological property is found to be different with the bottom L_1 phase. Our study provides basic data which may be useful for both fundamental research and practical applications of salt-free mixtures of cationic and anionic surfactants.

Acknowledgment. This work was supported by the NSFC (Grant No. 20625307 and 20533050, J.H.).

Supporting Information Available: Photos for samples within the $L_{\alpha v}$ two-phase region, phase-separated region, and L_α -1/ L_α -2/ L_1 three-phase region; rheological properties for samples with c_T of $30 \text{ mg} \cdot \text{mL}^{-1}$ and various ρ ; and more polarized micrographs of L_α phases. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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