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ARTICLE *in* LANGMUIR · OCTOBER 2009

Impact Factor: 4.46 · DOI: 10.1021/la902069w · Source: PubMed

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Phase Transition in Salt-Free Catanionic Surfactant Mixtures Induced by Temperature

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Received June 9, 2009. Revised Manuscript Received September 15, 2009

Aggregate transitions in salt-free catanionic surfactant mixtures of tetradecyltrimethylammonium hydroxide (TTAOH)/fatty acid were investigated as a function of surfactant concentration and temperature. Lauric acid (LA), myristic acid (MA), and palmitic acid (PA) were chosen for the current study. The TTAOH/LA mixture exhibited rich phase behavior at room temperature. With increasing total surfactant concentration (c_T), a bluish vesicular ($L_{\alpha v}$) phase, an isotropic micellar (L_1) phase, and a birefringent lamellar (L_α) phase were observed. Between the $L_{\alpha v}$ phase and the L_1 phase, a narrow L_α'/L_1 two-phase region was determined. With increasing temperature, a transition from the L_α phase to the L_1 phase was induced at higher c_T whereas at lower c_T an opposite transition from the L_1 phase to the $L_{\alpha v}$ phase was noticed. Thus surprisingly, we observed bilayer-to-micelle and micelle-to-bilayer transitions in the same catanionic surfactant system, both induced by the temperature increase. Replacing LA by MA and PA caused a continuous increase in the average Krafft point of the mixture. The $L_{\alpha v}$-phase region and phase-separated region become larger. Moreover, a single L_1-phase region was absent within the investigated temperature range.

Introduction

Surfactant molecules can self-assemble in water into a variety of aggregates, including micelles, vesicles, and lytropic liquid crystals. These molecular assemblies are not only of great fundamental interest but also have attractive potential applications. During the past few decades, considerable attention has been paid to the formation of molecular assemblies and phase transitions in cationic/anionic (catanionic) surfactant mixtures.[1−9] Because of electrostatic interactions between oppositely charged surfactant headgroups, cationic and anionic surfactants tend to form ion pairs when they are mixed in water. This phenomenon leads to an effective reduction of the area of surfactant headgroups and imparts extremely high surface activity to the ion pair. The surfactant ion pair behaves as a double-tailed amphiphile and tends to form molecular bilayers. Thus, vesicles can spontaneously form in catanionic mixtures in dilute aqueous solutions.[2,10,11] However, when the mixing molar ratio approaches 1 a precipitate will usually form as a result of the screening of the electrostatic interaction between oppositely charged surfactant groups by small counterions.[12] This is a big obstacle to further study and potential applications of catanionic surfactant mixtures. To solve this problem, different methods including extraction and dialysis have been proposed to eliminate the small counterions.[13−16] In recent years, so-called salt-free catanionic surfactant systems have been prepared by mixing alkyltrimethylammonium hydroxide with fatty acids in water.[12,17−25] In this case, small counterions can be partially eliminated (at a nonequimolar mixing ratio) or totally (at an equimolar mixing ratio) and the system exhibits diverse aggregate transitions upon changing the mixing ratio and total surfactant concentration.[25] Bicompatible salt-free catanionic surfactant mixtures

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made from choline cations and fatty acids have also been prepared.[26,27]

Of particular interest is the aggregate transitions induced by temperature in catanionic surfactant mixtures. Salt-free equimolar mixtures of cationic and anionic surfactants exhibit some peculiar properties in the solid state.[28−30] In bulk aqueous solutions, a vesicle-to-micelle transition induced by increasing temperature has been observed in the system of cetyltrimethylammonium hydroxynaphthalenecarboxylate (CTAHNC).[31−34] and hexadecyltrimethylammonium octylsulfonate (TASo).[35] In some catanionic surfactant mixtures where small counterions are still present, an opposite transition from micelles to vesicles has also been observed with increasing temperature.[36,37] Generally speaking, transitions between micelles and vesicles are governed by the curvature change of a surfactant monolayer or bilayer, which is further controlled by the surface charge density in the case of ionic surfactants. Although several examples of vesicle-to-micelle transition have been observed in catanionic surfactant systems with temperature rising, the dominating factors behind them vary from system to system. Thus, different explanations are usually given by different authors to explain similar phenomena in different systems. For example, Manohar et al. gave a mechanism for a Coulombic solid−fluid transition on a micellar surface to explain the vesicle-to-micelle transition in the cetyltrimethylammonium hydroxynaphthalenecarboxylate (CTAHNC)[31−33] system, and Marques et al. explained the vesicle-to-micelle transition by the dissociation of the octylsulfonate anion into bulk solution at higher temperature, which is believed to have a higher solubility in water compared to that of the hexadecyltrimethylammonium cation.[35] In cases of micelle-to-vesicle transition induced by temperature, the mechanism is still claimed to be unclear.[36,37] Taking into account these considerations, more work is needed to further clarify these interesting aggregate transitions induced by temperature in catanionic surfactant mixtures.

Recently, we have described the phase behavior of a salt-free catanionic surfactant system, tetradecyltrimethylammonium hydroxide (TTAOH)/lauric acid (LA)/H_2O.[25] At an equimolar mixing ratio of TTAOH and LA, a vesicular ($L_{\alpha v}$) phase forms that does not undergo an obvious transition with increasing temperature. This is quite different from the other salt-free catanionic surfactant systems with equimolar mixing ratios studied by Manohar et al. and Marques et al., which undergo a vesicle-to-micelle transition with increasing temperature.[31−35] A question arises as to whether aggregate transitions between micelles and bilayer structures can exist in this type of system. Here we show that by a suitable adjustment of the mixing molar ratio of LA to TTAOH ($\rho = n_{LA}/n_{TTAOH} = 0.88$) two distinct transitions (i.e., lamella to micelle and micelle to vesicle) can be induced by increasing temperature. The transitions strongly depend on the total surfactant concentration ($c_T = c_{TTAOH + LA}$). The presence of vesicles and lamellaes have been clearly identified by fluorescence microscopy observations and small-angle X-ray scattering (SAXS) measurements, respectively, and the lamella-to-micelle transition process was monitored by polarized microscopy observations. We also show that these phase transitions are influenced by the surfactant chain length, characterized by different fatty acids herein from lauric acid (LA) to myristic acid (MA) and palmitic acid (PA).

Experimental Section

Chemicals and Materials. Lauric acid (LA), myristic acid (MA), and palmitic acid (PA) with purities of >98% were purchased from Fluka and used without further purification. TTAOH stock solution was prepared following the procedures described previously.[25] Fluorescein was purchased from Riedel de Haen and used as received.

Preparation of TTAOH/Fatty Acid Mixtures. To three glass bottles each containing 100 mL of TTAOH stock solution the desired amounts of solid LA, MA, and PA were added. The mixing molar ratio of each fatty acid to TTAOH was fixed at 0.88. The samples were then kept at 50 °C in an oven to allow the acid−base reactions to occur, during which time frequent hand-shaking was performed. After all of the solid fatty acids were dissolved, the samples were kept in the oven for 1 more week to ensure the completion of the acid−base reactions. Afterwards, the samples were dried at 40 °C in the oven and the solid was collected for further use.

Phase Behavior Study. The phase behavior was recorded by visual inspection and crossed polarizers. The temperature, which was controlled with a water bath or an oven, was increased from 25 to 60 °C in increments of 5 °C. At each temperature, the samples were gently hand-shaken to get homogeneous solutions at the starting point and were then left to equilibrate for 2 weeks.

Fluorescence Microscopy Observations. Fluorescence microscopy observations were carried out on a Nikon Eclipse 50i microscope equipped with a black and white fluorescence camera. The samples were labeled with fluorescein at a final concentration of $\sim 10^{-5}$ M. A filter was used that can cut off excited light below 465 nm and above 495 nm.

SAXS Measurements. SAXS measurements were carried out using Cu Kα radiation of 0.15418 nm with a Bruker Nanostar system and a Vantec 2000 area detector. Samples were prepared by filling thin glass capillaries of 1.5 or 2.0 mm diameter, which were then flame-sealed immediately. The signal intensities were obtained through integration of the 2D patterns over the azimuthal angle. The temperature was changed from 23 to 30, 35, and 40 °C, respectively. For the sample with $\rho = 0.91$, SAXS measurement were carried out on the beamline 4B9A synchrotron radiation X-ray small-angle system at the Beijing Synchrotron Radiation Facility.

Polarized Microscopy Observations. Polarized microscopy observations were carried out on a Nikon Eclipse E400 microscope with a crossed polarizer equipped with a Linkam THMS 600 heating/cooling stage. The stage was controlled by a computer program called LinkSys 2.36 with temperature control of ±0.01 °C. The temperature was increased from 25 to 60 °C in increments of 5 °C. Samples were prepared between two circular glasses whose edges were immediately sealed with epoxy resin glue. The thickness of the sample was about 2 mm. We carried out observations both immediately after sample preparation and 2 days later to check the influence of the shear force introduced during sample preparation. Although the shear force was found to have some influence on the static texture of the L_α phase,[25] it did not have an obvious influence on the temperature-induced texture evolution during the L_α to L_1 phase transition.

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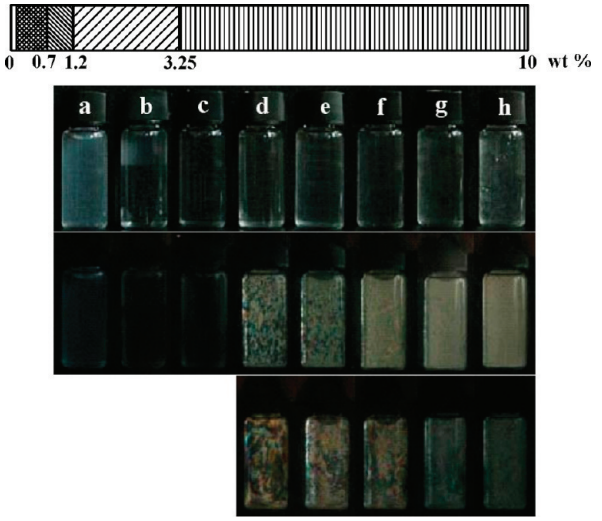

Figure 1. (Top) Phase diagram of the TTAOH/LA mixture in water with $\rho = 0.88$ recorded at room temperature (~22 °C). (□ region near 0 wt %) Phase-separated region; (cross-hatched region from > 0 to 0.7 wt %) $L_{\alpha v}$ phase; (diagonal lines from 0.7 to 1.2 wt %) L_α'/L_1 two-phase region; (diagonal lines from 1.2 to 3.25 wt %) L_1 phase; and (vertical-lined region from 3.25 to 10 wt %) L_α phase. (Bottom) Photographs of typical samples within different phase regions. From a to h, c_T (wt %) is 0.60, 0.98, 1.97, 3.77, 4.90, 6.06, 7.39, and 9.13, respectively. (First row) Without polarizers; (second row) with crossed polarizers; and (third row) photographs of samples in the L_α-phase region between crossed polarizers after gentle hand-shaking.

Results and Discussion

Phase Behavior at Room Temperature. The phase behavior of the TTAOH/LA mixture in water with $\rho = 0.88$ at room temperature together with photographs of typical samples within different regions are given in Figure 1. At high dilution ($c_T < 0.1$ wt %), some white flocculation was observed at the top of the bulk solution, which is nearly transparent. With increasing c_T, the area of the flocculation region shrinks and the bulk solution begins to be bluish, which is a typical feature of the vesicular ($L_{\alpha v}$) phase. At $c_T > 0.7$ wt %, the L_1 phase forms at the bottom, and the volume increases continuously with increasing c_T. At $c_T > 1.2$ wt %, the turbid upper phase (denoted as L_α') disappears and a single L_1-phase region is reached. The L_1 phase is transparent, optically isotropic, and very viscous. Rheological measurements revealed the presence of wormlike micelles.[25] At higher concentration, flow birefringence was also noticed. When c_T exceeds 3.25 wt %, a birefringent lamellar (L_α)-phase region is reached, and the birefringence in this region becomes stronger once disturbed by shear (bottom of Figure 1, third row).

Figure 2 gives a typical fluorescence micrograph of large vesicles in the $L_{\alpha v}$ phase. The vesicles are crowded and polydisperse, ranging from hundreds of nanometers to several micrometers. In some parts, two or more vesicles can contact each other (solid arrows). For vesicles formed by only one kind of ionic surfactant such as DDAB, the surface charge density of the bilayer is high. For catanionic vesicles, however, the bilayer contains both cationic and anionic components and the surface charge density is lower, making it easier for adjacent vesicles to get close. Together with globular vesicles, some deformed vesicles typically with cylindrical shapes are also noticed (empty arrows). Although FF-TEM and cryo-TEM are powerful techniques for capturing vesicles with submicrometer length scales, the fluorescence microscopy technique has the advantage of capturing vesicles typically with micrometer length scales, thus providing

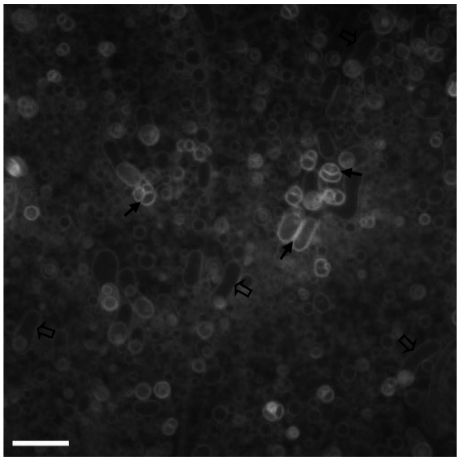

Figure 2. Typical fluorescence micrograph of large vesicles formed in the $L_{\alpha v}$ phase. $\rho = 0.88$ and $c_T = 0.4$ wt %. The bar corresponds to 10 μm.

an alternative method for studying catanionic vesicles. Other techniques such optical microscopy[32] or the cryo-SEM technique[35] were used to capture large catanionic vesicles in some catanionic surfactant mixtures. Compared to those techniques, however, the fluorescence microscopy method provides pictures with much higher contrast.

The structural details of the L_α phases were characterized by SAXS measurements, and a typical result recorded for the sample with $c_T = 9.13$ wt % is given in Figure 3. Three peaks were detected with relative position ratio to be 1:2:3, indicating a lamellar structure. The interlayer spacing d, calculated from the position of the first peak ($d = 2\pi/q_{max}$), was 19.5 nm. When c_T was lowered, a continuous increase in d was observed. For samples with c_T values of 6.59 and 4.90 wt %, d values of 22.7 and 36.0 nm were measured, respectively. The SAXS carried out on a sample with $\rho = 0.91$ and $c_T = 3.38$ wt % gave an even larger d value of 50.8 nm. At lower surfactant concentration, the number of bilayers is smaller than that at higher surfactant concentration, accounting for the swelling of the L_α phase and the increase in d value with the continuous decreasing in c_T. When c_T was lowered, the difficulty in obtaining relative peaks in the lamellar phase increased significantly. This could be ascribed to the decrease in the bilayer number density and more pronounced lamella fluctuation at lower c_T. Compared with the case at higher c_T as shown in Figure 3, the peaks obtained at lower c_T were usually broad and in some cases even bimodal (Supporting Information). The structure of these peaks indicated that some other ordered structures coexisted with the L_α phase close to the L_α/L_1 phase boundary. Similar problems were pointed out by other authors.[38−41] For example, Hoffmann et al. pointed out that the L_α phase can coexist with the vesicular or L_3 phase in the alkyldimethylamine oxide/heptanol/water system,[38] and Dubois et al. found that the lamellar structure can coexist with disklike micelles in the cetyltrimethylammonium hydroxide/myristic acid/water system.[39]

Between the $L_{\alpha v}$ phase and single L_1 phase an L_α'/L_1 two-phase region forms with a turbid L_α' phase at the top. Examinations of the weight percent of surfactants involved in the upper and bottom phases for a sample with $c_T = 0.8$ wt % indicates that

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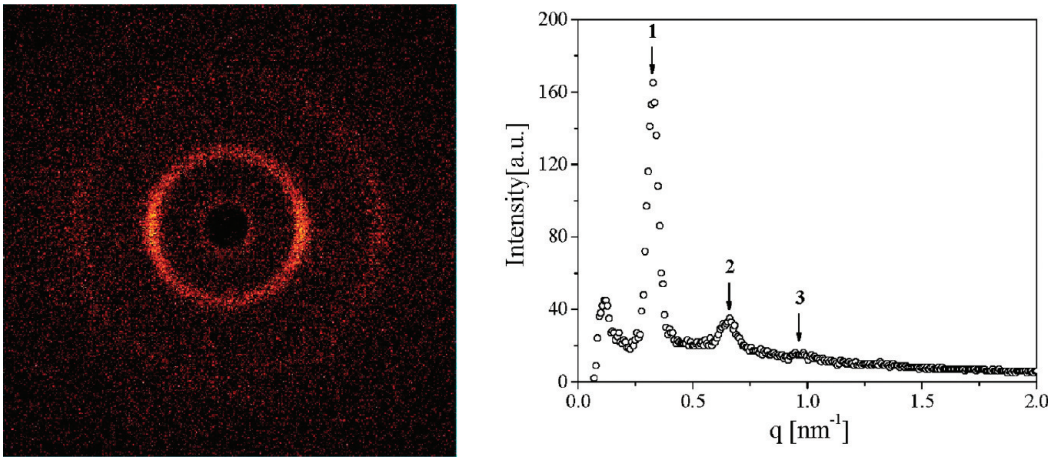

Figure 3. (Left) Two-dimensional SAXS diffraction pattern and (right) corresponding scattering peaks after the signal integral for an L_α phase formed by the TTAOH/LA mixture in water with $\rho = 0.88$ and $c_T = 9.13$ wt %.

the individual c_T is 1.661 wt % for the upper phase and 0.363 wt % for the bottom phase; therefore, the upper L_α' phase was much richer in surfactant than the bottom L_1 phase. Fluorescence microscopy observations revealed that in the upper L_α' phase very crowded vesicles were formed. Surprisingly, vesicles have also been detected in the bottom L_1 phase, where the vesicles are larger and more dispersed than in the upper L_α' phase (Supporting Information). In contrast, in the single L_1 phase region no vesicles were found at all. This indicates that the bottom phase within the L_α'/L_1 two-phase region is not a real L_1 phase but rather a mixture of micelles and vesicles.

Aggregate Transitions Induced by Temperature. Figure 4A shows the phase behavior as a function of surfactant concentration and temperature for the TTAOH/LA mixture in water with $\rho = 0.88$. With increasing temperature, a transition from the L_α phase (lamella) to the L_1 phase (micelle) is induced at higher c_T whereas at lower c_T an opposite transition from the L_1 phase (micelle) to the $L_{\alpha v}$ phase (vesicle) is noticed. To the best of our knowledge, this is the first time that both bilayer-to-micelle and micelle-to-bilayer transitions have occurred in the same catanionic surfactant system induced by a temperature increase. During the lamella-to-micelle transition, the L_1 phase forms from the bottom of the L_α phase and its volume increases gradually with increasing temperature. The higher the c_T of the L_α phase, the higher the temperature at which the L_α to L_1 phase transition occurs. Thus, the volume fraction of the upper L_α phase increases with increasing c_T at a fixed temperature and decreases with increasing temperature at a fixed c_T (Supporting Information).

The transition from micelles to vesicles, which is separated by an L_α'/L_1 two-phase region, is not obvious below 45 °C. Above 45 °C, the $L_{\alpha v}$-phase region expands to higher c_T at the expense of the adjacent L_α'/L_1 two-phase region. Correspondingly, the L_α'/L_1 two-phase region expands to higher c_T at the expense of the adjacent L_1-phase region. Even within the L_1-phase region, which is usually transparent, a small amount of white flocculation formed above 45 °C. It could be easily redispersed by gentle hand-shaking, making the L_1 phase more or less turbid. This clouding phenomenon is probably due to the formation of aggregated large multilamellar vesicles within the L_1 phase with increasing temperature.

Replacing LA by MA and PA causes obvious changes in the phase behavior, as shown in Figure 4B,C. As the chain length of fatty acid increases, both the $L_{\alpha v}$ phase region and the phase-separated region broaden while the L_α-phase region shrinks. Moreover, for MA and PA, a single L_1-phase region is missing. With a longer chain length of fatty acid, a corresponding increase in the average Krafft point is also induced. Whereas the TTAOH/LA mixture has an average Krafft point well below room temperature, the TTAOH/MA and TTAOH/PA mixtures have average Krafft points of around 25 and 33 °C, respectively. The average Krafft point shows a dependence on the surfactant concentration. Similar observations have also been made in mixtures of didodecyldimethylammonium (DDAB) with some anionic surfactants such as sodium dodecylsulfate (SDS)[42−44] or sodium dioctylsulfosuccinate (AOT)[45] and were ascribed to the counterion effect[46] because a change in surfactant concentration is always accompanied by a change in counterion concentration.

Unlike the phase-separated region in the TTAOH/LA mixture that is dominated by an L_α/L_1 two-phase region, the phase-separated region in the TTAOH/MA and TTAOH/PA mixtures is dominated by the L_α'/L_1 two-phase region where the upper phase is nearly opaque. At higher temperatures, however, the opaque L_α' phase becomes unstable and transforms gradually with time to a transparent L_α phase and a flocculated phase, which is the third condensed phase at the phase boundary. The mechanism behind the L_α'-to-L_α phase transition is currently not very clear. It is probably controlled by kinetic factors because of the thermodynamically unstable L_α' phase. In fact, on the basis of previous papers, we could expect pronounced metastability in surfactant systems.[47,48]

Polarized Microscopy Observation and SAXS Measurements. Because the L_α phase is birefringent and the L_1 phase is optically isotropic, the lamella-to-micelle transition can be well monitored by temperature-controlled polarized microscopy observations. Typical results carried out on a sample with $c_T = 5.58$ wt % are given in Figure 5. One can see that the texture of the L_α phase fades with increasing temperature. More observations revealed that texture fading occurs at higher temperature for the sample with a higher c_T (Supporting Information), which is consistent with the above-mentioned phase-behavior study.

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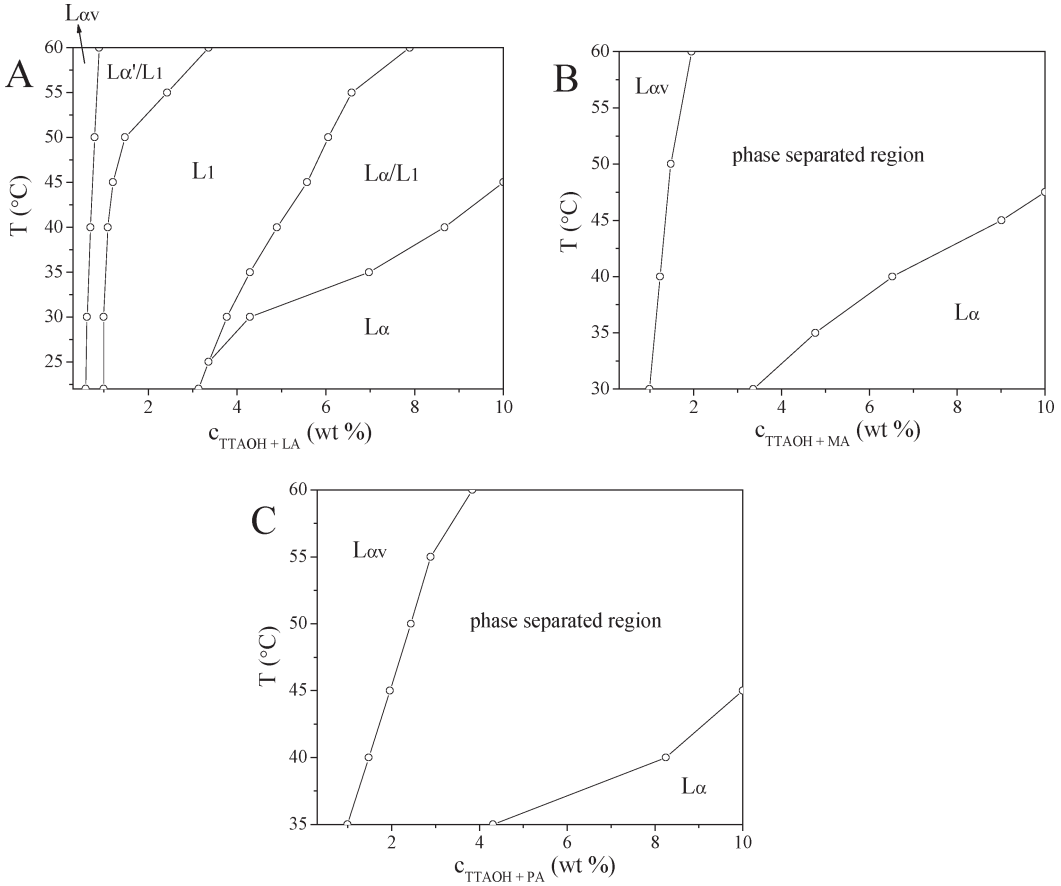

Figure 4. Phase diagram of (A) the TTAOH/LA mixture, (B) the TTAOH/MA mixture, and (C) the TTAOH/PA mixture in water as a function of surfactant concentration and temperature. The mixing molar ratio of fatty acid to TTAOH is 0.88 in all cases. We prepared samples in the c_T range of 0.3−10 wt % in increments of 0.5 wt %. Near the phase-transition boundaries, additional samples were prepared to determine the boundaries more precisely.

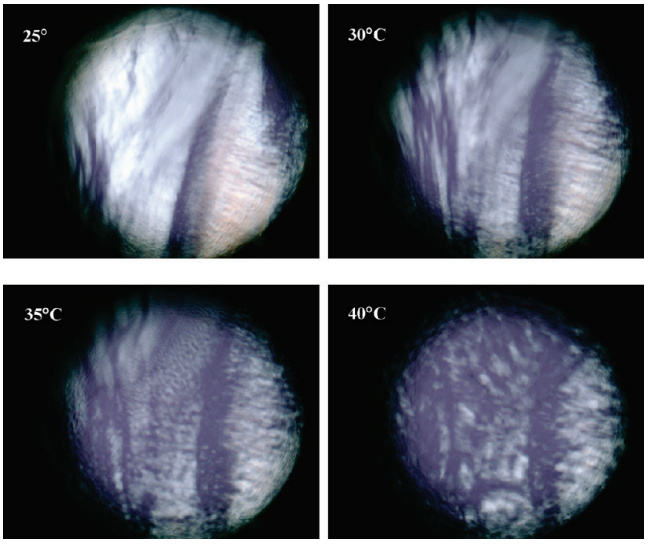

Figure 5. Evolution of textures induced by temperature for a typical sample within the L_α phase region. c_T = 5.58 wt %. Images were obtained from the same region of the sample, and the magnification is the same with a total width of 2.7 mm.

SAXS measurements were carried out at different temperatures for a typical L_α phase with c_T = 9.13 wt %, and the results are summarized in Figure 6. The highest temperature is 40 °C, which is well below the L_α-to-L_1 phase-transition point for this sample (Figure 4). The temperature-induced swelling of the L_α phase did

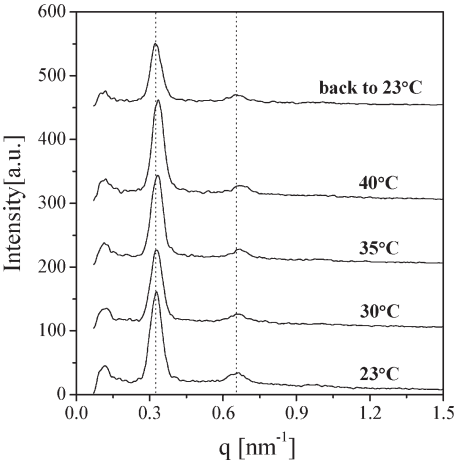

Figure 6. SAXS results recorded at different temperatures for a typical L_α phase with c_T = 9.13 wt %. The intensity for the bottom curve is the real value, and the other curves moved along the y axis for better clarity. The two straight dotted lines are guides to the eyes.

not occur because d did not change much within the selected temperature range. Instead, the peak position slightly moved to higher q values at higher temperatures, indicating a continuous decrease in d with increasing temperature. For example, the d value at 23 °C was 19.5 nm and changed gradually to 18.8 nm at 40 °C. When the sample was cooled from 40 °C back to 23 °C,

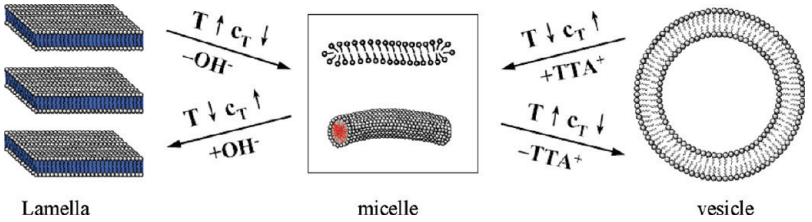

Figure 7. Schematic illustration of the aggregate transition between lamella, micelles, and vesicles induced by temperature and surfactant concentration in the TTAOH/LA mixture with TTAOH in slight excess. For simplicity, a rodlike micelle and unilamellar vesicle are shown here. However, wormlike micelles and multilamellar vesicles may also be present.

the peak position and hence d recovered to the original value. The decrease in d with increasing temperature can be ascribed to the change in state of the alkyl chains within the surfactant bilayer. Although the alkyl chains are more ordered at room tempreature, they will become more and more disordered with increasing temperature. The thickness of the bilayer formed by the disordered alkyl chains is smaller than that formed by the ordered alkyl chains,[49] accounting for the decrease in d at higher temperatures. When the temperature is changed back to the initial value, the alkyl chains also change from the disordered state back to the ordered state, which leads to a complete recovery of d.

Mechanism behind the Lamella-to-Micelle and Micelle-to-Vesicle Transitions. From the point of view of curvature, the lamella-to-micelle and micelle-to-vesicle transitions proceed in opposite ways; therefore, the mechanisms behind them should be different. In the following text, we will show that the lamella-to-micelle transition may be explained through counterion binding whereas the micelle-to-vesicle transition can be understood by the variation of components involved in the aggregates.

Generally speaking, aggregate transitions in surfactant solutions can be explained by the theory of the critical packing parameter $p = V/la_0$, where p is the critical packing parameter of a given surfactant molecule, V and l are the volume and length of the hydrophobic alkyl chain, respectively, and a_0 is the area of the hydrophilic headgroup.[50] The value of p is closely related to the spontaneous curvature of monolayers or bilayers formed by a given surfactant, which subsequently governs the type of aggregate formed. For an ionic surfactant, p shows a strong dependence on the electrostatic interactions between surfactant molecules, which is mainly governed by the binding of small counterions. In the case of a catanionic surfactant system such as the TTAOH/LA mixture, p can be also changed significantly because of the strong association between the two oppositely charged surfactant headgroups, which will cause a significant decrease in a_0. When the mixing ratio between LA and TTAOH is 1, the surfactant ion pairs can act as a double-tailed surfactant with a p value of around 1 and can organize themselves into vesicles within a wide c_T range.[25]

When TTAOH is in excess as in the current case, small counterions of OH^- are present. In some cases, lamellar phases form at room temperature (c_T > 3.25 wt % in current case), and the excess OH^- should dissociate into bulk water because TTAOH is known as a strong base. Also in studies of double-chained amphiphiles with OH^- as counterions,[51−53] OH^- was found to have a stronger affinity for water and to sit much further from a charged surface than chloride or bromide ions. However, we speculate here that some of them may still exist near the lamella and create a negative charge cloud that can lower the surface charge density of the lamella. With increasing temperature, these negative charges begin to move further away, leaving the lamella more positively charged. Driven by the increase in curvature, the transition from lamella to micelle is induced. Because the "dissociation" of the negative charges near the lamella is a continuous process, the lamella-to-micelle transition is also continuous. In some region, lamellas and micelles coexist, forming an L_α/L_1 two-phase region.

The micelle-to-vesicle transition, which occurs at lower c_T, can be explained by the variation of components involved in the aggregates. The TTAOH/LA mixture with TTAOH in excess is equivalent to a mixed system of a double-tailed surfactant and an excess single-tailed surfactant. The micelles formed in the L_1 phase consist of both surfactant ion pair TTA^+L^- and excess single-tailed surfactant ion TTA^+. Because TTAOH has a much higher critical micellar concentration (cmc) than surfactant ion pair TTA^+L^- and the concentration of TTAOH unimers in water can be orders of magnitude higher than that of TTA^+L^-, TTAOH may dissociate gradually into bulk solution with increasing temperature. This will lower the surface charge density and make the micelle transform to aggregates that are not as greatly curved (i.e., vesicle). Similar mechanisms have also been proposed for other systems such as lipid/detergent,[54] lecithin/bile salt,[55] and DDAB/SDS[44] mixtures. At higher temperature, the dissociation of surfactant ion pairs also becomes more obvious ($TTA^+L^- \rightarrow TTA^+ + L^-$), which can increase the number of free TTA^+ and facilitate the dissolution of excess TTA^+ from aggregated form to bulk aqueous solution. A schematic illustration of the lamella-to-micelle and micelle-to-vesicle transitions is shown in Figure 7.

Because the micelle-to-vesicle transition observed in other catanionic surfactant systems also occurrs in nonequimolar mixtures, it is worth mentioning that they probably share the same mechanism as mentioned above. Thus, the mechanism of transitions shown in Figure 7 is also expected to work in other catanionic surfactant systems where the micelle-to-vesicle transition was also observed.[36,37] For charged aggregates with a fixed surfactant composition, the electrostatic repulsion between aggregates usually increases at higher temperature because of the dissociation of small counterions. However, the zeta potential was found to be almost constant at different temperatures in mixed system of SDS/dodecyltributylammonium bromide where SDS is in excess.[56] This is a proof of dissociation of SDS molecules into bulk aqueous solution with increasing temperature, which can lower the surface charge density of the aggregate and compensate for the opposite effect of small counterion dissociation.

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Conclusions

In summary, we have investigated the aggregate transitions in salt-free catanionic surfactant mixtures as a function of surfactant concentration and temperature. Typically in the TTAOH/LA mixture with $\rho = 0.88$, two dominating aggregate transitions have been detected. With increasing temperature, an L_α-to-L_1 phase transition via an intermediate L_α/L_1 two-phase region occurs at higher c_T, which corresponds to an aggregate transition from lamella (open bilayer) to micelle. At lower c_T, an L_1-to-$L_{\alpha v}$ phase transition is induced via an intermediate L_α'/L_1 two-phase region, which corresponds to an opposite aggregate transition from micelle to vesicle (closed bilayer). Although bilayer-to-micelle transition and micelle-to-bilayer transitions have been observed separately in other surfactant systems, they are seldom present in the same system. The TTAOH/LA mixture is shown to be a perfect model system for investigating these transitions, and this is the first system to exhibit both bilayer-to-micelle and micelle-to-bilayer transitions with increasing temperature. Similar aggregate transitions have been observed in the TTAOH/MA and TTAOH/PA mixtures. The replacement of LA by MA or PA, which have longer chain lengths than LA, induces a small difference. This includes a higher average Krafft point, a wider $L_{\alpha v}$, a phase-separated region, the absence of a single L_1-phase region, and a more pronounced L_α'-to-L_α phase transition within the phase-separated region.

Acknowledgment. This work was supported by the project operated within the Foundation for Polish Science Team Programme cofinanced by the EU "European Regional Development Fund" TEAM/2008-2/2 and also by the Human Frontiers Science Program Organization and a MISTRZ grant from FNP. Dr. Hao is grateful for financial support by the NSFC (grant no. 20625307) and the National Basic Research Program of China (973 program, 2009CB930103). We are grateful to Prof. Garstecki for useful comments and discussions.

Supporting Information Available: Additional SAXS results on lamellar phases, fluorescence microscopy and polarized microscopy images, and evolution of the volume fraction of the upper L_α phase as a function of surfactant concentration and temperature within the phase-separated region. This material is available free of charge via the Internet at http://pubs.acs.org.