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Phase Behavior and Properties of Reverse Vesicles in Salt-Free Catanionic Surfactant Mixtures

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Salt-free 1:1 cationic/anionic (catanionic) surfactant mixture tetradecyltrimethylammonium laurate (TTAL) could be prepared by mixing equimolar tetradecyltrimethylammonium hydroxide (TTAOH) and lauric acid (LA) in water. Given the condition of suitable range of weight fraction of TTAL in total surfactant, $\rho = W_{TTAL}/(W_{TTAL} + W_{LA})$, and at existence of a small amount of water, it was found that the mixtures of so-obtained TTAL and LA could spontaneously form stable reverse vesicles in various organic solvents including toluene, *tert*-butylbenzene, and cyclohexane. The reverse vesicle phase shows a blue color against room light and exhibits strong birefringence under polarized microscope. The reverse vesicles are very sensitive to temperature change. Increasing temperature could make the ρ values within which reverse vesicles were constructed move to higher values. In organic solvents of alkanes such as *n*-heptane, reverse vesicles could still form but become unstable upon time and centrifugation. Increasing temperature could accelerate phase separation, and finally a gel-like bottom phase was usually observed. Interestingly, the stable reverse vesicles formed by so-called salt-free catanionic surfactant mixtures still show some resistance against adding inorganic salts. They can trap inorganic ions such as Zn^{2+} and S^{2-} into their hydrophilic layers. This opens the door for template applications of reverse vesicles to prepare inorganic nanoparticles.

Introduction

Normal vesicles are uni- or multimolecular bilayers with hydrophobic parts inside and hydrophilic parts outside formed by lipids or surfactants in aqueous solution. Since their description in 1964,[1] vesicles have received considerable interest both fundamentally and industrially because of being good candidates for drug delivery and mimicking biological membranes.[2-4] Vesicles can be constructed by dispersing phospholipid lamellar phases in water with the help of mechanical energy[1] or by diluting a mixed micellar solution or the mixtures of lecithin and a bile salt (or another polar amphiphile).[5-8] In 1989, Kaler et al. reported the spontaneous formation of stable vesicles in dilute aqueous solution of cationic and anionic (catanionic) single-tailed surfactant mixtures,[9] which triggered a flame in the study of catanionic surfactant mixtures in the following years. However, as the concentrations of cationic and anionic surfactants increase, the excess salt formed by their counterions can greatly screen the electrostatic interaction between aggregate films and lead to precipitate formation, especially when the stoichiometry between the cationic and anionic components is exactly 1.[10] This has greatly hindered further study and applications of catanionic surfactant mixtures. In recent years, a successful way has been found to eliminate the excess salt by using OH^- and H^+ as counterions of cationic and anionic surfactants, respectively, and by mixing them in equimolar ratio.[11-13] The so-obtained salt-free catanionic surfactant mixtures in solution are stable at very high concentration compared to conventional salt-containing ones, and recent studies revealed
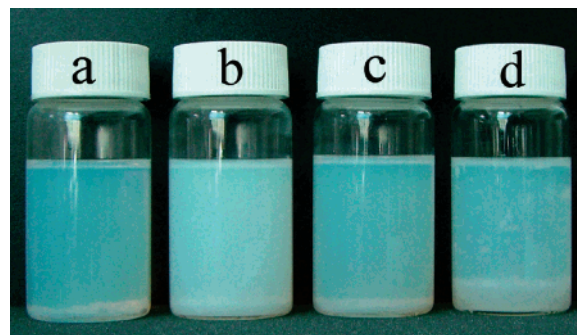
Figure 1. Photos of four typical samples with upper-blue reverse vesicle phases. Each sample contains 1 mL of H_2O and 14 mL of organic solvent. (a) In toluene, $\rho = W_{TTAL}/(W_{TTAL} + W_{LA}) = 0.90$, $W_{TTAL+LA} = 0.3762$ g; (b) in toluene, $\rho = 0.92$, $W_{TTAL+LA} = 0.3588$ g; (c) in *tert*-butylbenzene, $\rho = 0.82$, $W_{TTAL+LA} = 0.4183$ g; (d) in cyclohexane, $\rho = 0.90$, $W_{TTAL+LA} = 0.3610$ g.

the existence of fascinating aggregates such as disclike micelles[12a] and regular hollow icosahedra aggregates[12b] besides uni- and multilamellar vesicles.[13] One of them is also found to be able to greatly enhance the solubility of fullerene C_{60} in water.[13f,g] In comparison with the study of salt-free catanionic surfactants in aqueous solutions, however, their properties in nonaqueous media were rarely known.[14]

As the counterparts of normal vesicles, reverse vesicles were formed in nonaqueous solutions with hydrophilic parts inside and hydrophobic parts outside. They were first constructed by adding a small amount of water to the mixtures of tetraethyleneglycol dodecyl ether ($R_{12}EO_4$) and dodecane as reported by Kunieda et al. in 1991.[15,16] Reverse vesicles were also observed in other similar systems.[17-29] However, these reverse vesicles typically formed by nonionic surfactants in liquid hydrocarbons

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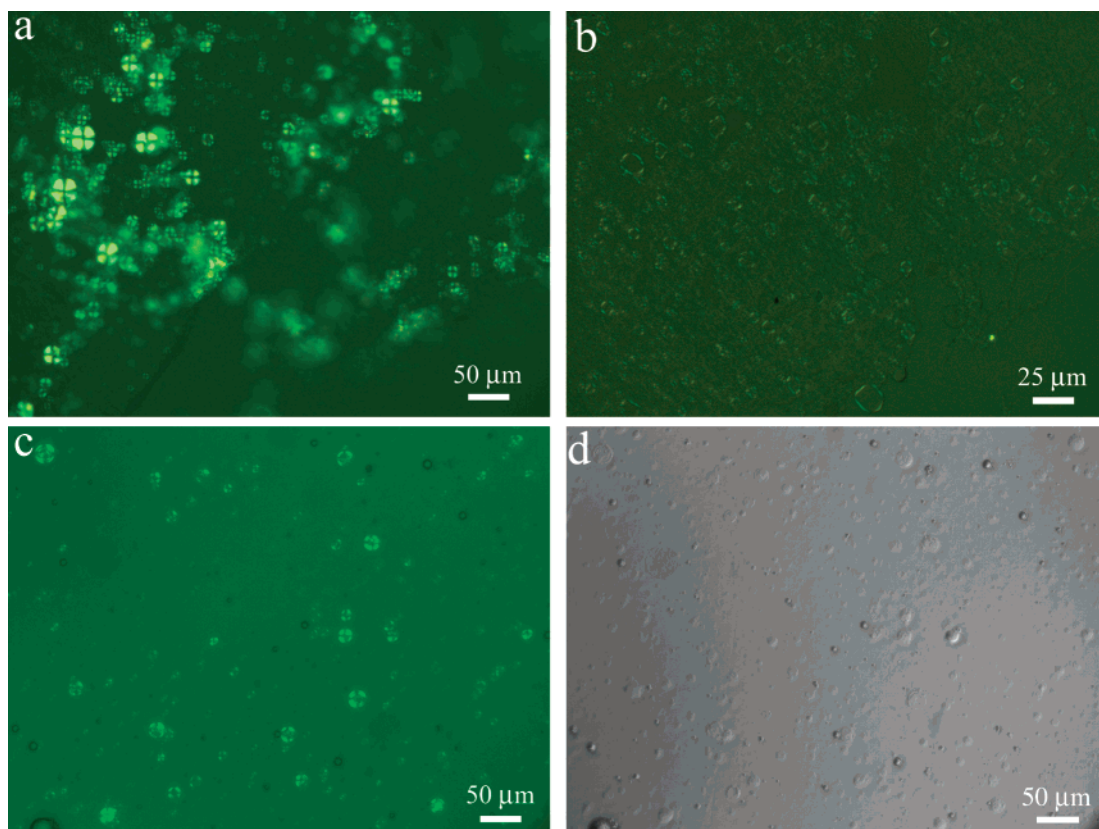
Figure 2. Typical polarized micrographs of reverse vesicles formed in toluene (a, obtained on the upper bluish phase of sample a in Figure 1), *tert*-butylbenzene (b, obtained on the upper bluish phase of sample c in Figure 1), and cyclohexane (c, d, obtained on the upper bluish phase of sample d in Figure 1 with and without polarizers), respectively.

TABLE 1: Temperature at Which 0.1 g of TTAL Dissolved Totally in 1.5 mL of Each Organic Solvent and Weight Fraction of TTAL in Total Surfactants, $\rho = W_{TTAL}/(W_{TTAL} + W_{LA})$, within Which Reverse Vesicles Formed; Stability of Reverse Vesicles Was Also Included

solvent	temperature range of TTAL total dissolution	weight fraction range of reverse vesicle formation	stability
Benzene	35 °C < T < 40 °C	0.86−0.88	stable
Toluene	35 °C < T < 40 °C	0.86−0.92	stable
tert-butylbenzene	55 °C < T < 60 °C	0.78−0.82	stable
Cyclohexane	slightly above 60 °C	0.86−0.91	stable
n-heptane	>60 °C	0.86−0.88	unstable
n-octane	>60 °C	0.82−0.86	unstable

were usually constructed by an external energy and were rather unstable, i.e., they were usually constructed by handshaking a two-phase system containing liquid crystals and excess oil and often rebounded to the initial state if keeping for a period of time. Recently, we have successfully constructed reverse vesicles of salt-free catanionic surfactant mixtures TTAL/LA in toluene at the presence of a small amount of water.[14] Similar to normal vesicles of catanionic surfactant mixtures in aqueous solutions, these reverse vesicles formed spontaneously and were very stable at room temperature.[14] Herein we report the phase behavior and properties of reverse vesicles formed by salt-free catanionic surfactant mixtures TTAL/LA in various organic solvents. The possible applications of reverse vesicles as templates to synthesize inorganic nanoparticles were also tried and discussed.
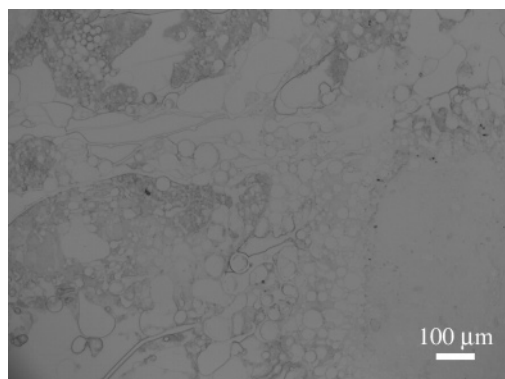
Experimental Section

Chemicals and Materials. Tetradecyltrimethylammonium bromide (TTABr, analytical grade) was purchased from Merck and used without further purification. Lauric acid (LA, chemical grade, >98%) was purchased from Shanghai Shiyi Chemicals

Reagent Co., Ltd., and used as received. All the other reagents including various organic solvents and inorganic salts were analytical grade and used as received.

Preparation of Salt-Free 1:1 Catanionic Surfactant TTAL. Tetradecyltrimethylammonium hydroxide (TTAOH) stock solution was prepared from TTABr aqueous solution by anion exchange (Ion exchanger III, Merck) followed the procedures described previously.[13] The concentration was determined to be 135.3 mmol·L^{-1} by acid−base titration by using standard 111.3 mmol·L^{-1} HCl aqueous solution. To a portion of this stock solution, equimolar solid LA was added. The sample was then heated to ~50 °C with frequent shaking to accelerate LA dissolution and subsequent reaction process (TTAOH + LA = TTAL + H$_2$O). After LA was consumed totally as monitored by simple visual inspection, the sample was further stored at ~50 °C for one more week ensuring complete reaction and then dried in an oven below 50 °C to get a solid salt-free 1:1 catanionic surfactant TTAL mixture.

Solubility of TTAL and LA in Various Organic Solvents. Various organic solvents including benzene, toluene, *tert*-butylbenzene, xylene, *n*-heptane, *n*-octane, decane, cetane,

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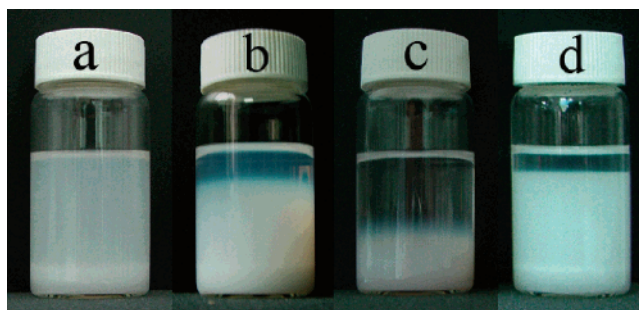*J. Phys. Chem. B, Vol. 112, No. 12, 2008* **3707**

Figure 3. A typical micrograph of reverse vesicle phase obtained without polarizers after passing the upper bluish phase of sample a in Figure 1 through a 0.22-μm filter.

Figure 4. Phase behavior variation of reverse vesicles formed in *n*-heptane as a function of time and centrifugation, respectively. (a) Newly prepared; (b) kept at room temperature for about 2 weeks; (c) kept at room temperature for about 2 months; (d) sample a after centrifugation at 1500 rpm for about 15 min. The sample contains 1 mL of H$_2$O, 14 mL of *n*-heptane, and 0.3837 g of surfactants with $\rho =$ 0.87, respectively.

cyclohexane, ethanol, *n*-octanol, tetrahydrofuran, acetonitrile, chloroform, carbon tetrachloride, diethyl ether, carbon disulfide, and dimethyl sulfoxide were selected for solubilizing TTAL and LA. Typically 0.1 g of solid TTAL or LA was weighed accurately to each bottle containing 1.5 mL of the corresponding organic solvent. The samples were then stored at desired temperatures from 25 to 60 °C with the help of a water bath for at least 2 days (the temperature jump was 5 °C), during which shaking was performed several times to accelerate the dissolution equilibrium. The dissolution situation of TTAL and LA after each temperature variation was then inspected carefully and recorded.

Phase Behavior Study of TTAL/LA in Various Organic Solvents. First experiments needed to be designed to determine the range of TTAL weight fraction in total surfactants ($\rho = W_{TTAL}/(W_{TTAL} + W_{LA})$) for the selected organic solvents within which reverse vesicles formed. In our experiments, the ρ value was varied by every 2% typically from 0.70 to 0.98 by accurately weighing a desired amount of solid TTAL and LA to each bottle. The weight of total surfactants was fixed at 0.025 g, and the total volume of the sample after added water and each organic solvent was fixed at 1.5 mL, respectively. The volume ratio of added water to each organic solvent was fixed at 1:10. Then the samples were stored at room temperature (~25 °C) for at least 2 weeks before phase behavior was determined.

After determining the range of ρ value for each selected organic solvent within which reverse vesicles formed, the temperature-induced phase behavior was investigated. To get a better observation of the phase behavior, samples were prepared freshly with ρ value varied by every 1% and total volume of each sample increased to be 4 mL. The weight of total surfactants was increased to be 0.1 g correspondingly, while the volume ratio of added water to each organic solvent was maintained at 1:10. Then the samples were stored at each desired temperature from 25.0 to 40.0 °C with the help of a water bath for at least 2 weeks (the temperature jump was 5 °C) before the temperature-induced phase behavior was determined. Finally the samples with the sample organic solvents were mixed every three neighboring samples with final volume modified to be 15 mL by adding each organic solvent and further kept for two weeks at 25.0 and 40.0 ± 0.1 °C, respectively, for taking photos.

Characterizations of Reverse Vesicles. Polarized microscopy observations of reverse vesicles were carried out on an AXIOSKOP 40/40 FL (ZEISS, Germany) microscope. Samples were prepared by dropping several drops of reverse vesicle solutions onto a thin glass slice, which was then covered by another glass slice, or by dropping some drops of reverse vesicle

solutions into a 1 mm thick trough, which was then sealed to avoid solvent evaporation.

Small-angle X-ray scattering (SAXS) experiments were carried out at Beamline 4B9A at the Beijing Synchrotron Radiation Facility, using a SAXS apparatus constructed at the station. A detailed description of the spectrometer was given elsewhere.[30]

Results and Discussion

Solubility of TTAL and LA in Various Organic Solvents. The solubility of TTAL and LA in various solvents is very important for determining which organic solvents should be selected to construct reverse vesicles because, if TTAL and LA are both soluble in certain organic solvents or both insoluble in them, construction of reverse vesicles would fail. In other words, the best combination of surfactant mixtures to construct reverse vesicles is that one is soluble while another is insoluble in certain organic solvents. This is verified by the fact that salt-free catanionic surfactant mixture of TTAL and LA could not form reverse vesicles in ethanol, tetrahydrofuran, chloroform, and acetonitrile, which are good solvents for both TTAL and LA. This conclusion is also consistent with the rule pointed out by Kunieda et al. that if highly hydrophilic surfactant or ionic surfactant was used to construct reverse vesicles, addition of another hydrophobic surfactant was necessary to monitor the total HLB values of surfactant mixtures.[17,18]

LA is soluble in all the selected organic solvents at room temperature. For 0.1 g of solid LA in 1.5 mL each of organic solvent, LA dissolved immediately or within minutes only after gentle shaking. For 0.1 g solid TTAL in 1.5 mL each of organic solvent, it was found the solid dissolved totally at room-temperature in polar organic solvents including tetrahydrofuran, acetonitrile, chloroform and alkyl alcohols with carbon numbers less than 8. In other investigated organic solvents, the solid could not dissolve totally at room temperature, and the dissolution process was greatly influenced by the type of solvent and temperature. In carbon disulfide, an interesting color change was also observed, but that is not the main subject to be discussed here. The detailed dissolution information of 0.1 g of TTAL in 1.5 mL of selected benzene derivatives and alkanes, which were subsequently selected to construct reverse vesicles were included in Table 1.

Reverse Vesicle Formation of TTAL/LA in Six Selected Organic Solvents. In our experiments, 11 organic solvents were selected to construct reverse vesicles. They could be divided into mainly two kinds: benzene derivatives and alkanes. In each
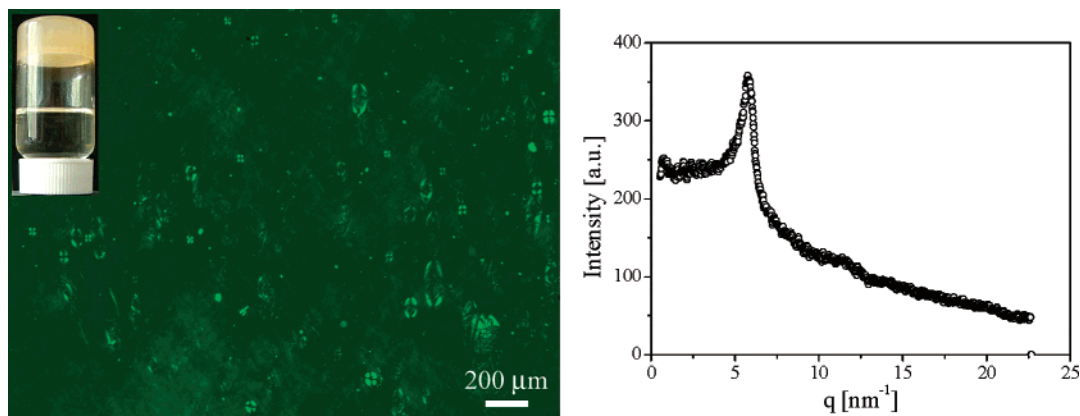
Figure 5. Typical polarized micrograph and SAXS result of the bottom gel-like phase formed in *n*-heptane as shown inset. The sample contains 1 mL of H_2O and 14 mL of *n*-heptane with $\rho = 0.91$ and $W_{TTAL+LA} = 0.4$ g.

pure solvent, the reverse vesicle could not form, which was consistent with the literature and our previous results.[14] TTAL and LA would deposit at the bottom, and clearly, transparent upper solution forms at the top. After addition of a small amount of water, however, bluish reverse vesicle phases would be observed. It was found the mixture of TTAL and LA was easy to form reverse vesicles in all the three tested benzene derivatives with only one aryl including benzene, toluene, and *tert*-butylbenzene, while attempts to construct reverse vesicles in xylenes failed within the investigated weight fraction range of TTAL in total surfactants, ρ, varied from 0.70 to 0.98 in our experiments. Reverse vesicles could also be constructed in alkanes including cyclohexane, *n*-heptane, and *n*-octane, while in other tested alkanes including *n*-pentane, *n*-hexane, *n*-decane, and *n*-cetane, no obvious bluish reverse vesicle phases were observed within the investigated weight fraction range of ρ. Finally we successfully prepared reverse vesicle phases in 6 among 11 selected organic solvents. The range of ρ within which reverse vesicles formed were summarized in Table 1. Although reverse vesicles could form in the six organic solvents mentioned above, their properties were different, as will be discussed in detail in the following sections separately.

Spontaneous Formation of Stable Reverse Vesicles in Benzene, Toluene, *tert*-Butylbenzene, and Cyclohexane. The stability of reverse vesicles depended greatly on the kind of organic solvent used. It was found reverse vesicles could form spontaneously in benzene, toluene, *tert*-butylbenzene, and cyclohexane. Once formed, they were very stable and could be stored at room temperature for more than a year (till this work was completed) without obvious changes occurring. The samples could also resist centrifugation up to 3000 rpm for more than half an hour. This makes one recall the spontaneous formation and high stability of normal vesicles formed by cationic and anionic single-tailed surfactant mixtures in dilute aqueous solutions.[9] It seems nature always has its symmetry not only of shape but also of process, i.e., not only catanionic surfactant mixture can spontaneously form normal vesicle in aqueous solutions, but also can they form reverse vesicles spontaneously in organic solvents. Four typical samples of reverse vesicles formed in toluene, *tert*-butylbenzene, and cyclohexane were given in Figure 1.

The blue reverse vesicle-phase exhibits strong birefringence under polarized microscope, which was consistent with our previous reports.[14] Typical polarized micrographs for reverse vesicles formed in toluene, *tert*-butylbenzene, and cyclohexane were given in parts a–c of Figure 2, respectively. The observed reverse vesicles, whose dimensions were usually in the range

of several to tens of micrometers, show bright crosses under a polarized microscope. These crosses were characteristic features of lamellar phases and corresponding to regular or deformed spherical reverse vesicles. Interestingly the reverse vesicles could still be seen under microscope without using polarizers. A typical micrograph of reverse vesicles formed in cyclohexane without polarizers was also given in Figure 2d. This characteristic feature of reverse vesicles formed by salt-free catanionic surfactant mixtures was also consistent with our previous reports[14] (more micrographs could be seen in Supporting Information).

From Figure 2, one can also see that the quantity of reverse vesicles is usually large and that they tend to adhibit with each other. This gives an indirect evidence of effective formation of reverse vesicles of catanionic surfactant mixtures in organic solvents, which reminds one again of their effective formation of normal vesicles in aqueous solutions with the feature of a rather low critical micellar concentration (cmc). Of course, the observed phenomenon of conglutination of the reverse vesicles might also occur during sample preparation process for polarized microscope observations. The inevitably solvent evaporation during the course of observation might also play a role.

After passing through a 0.22-μm nylon filter, giant reverse vesicles with micrometer dimensions could still be seen by polarized microscope. Probably there was a rapid recovery and reformation of the reverse vesicles, which usually have a diameter of several or tens of micrometers as characterized by polarized microscopy after passing through the filter, though they were instantaneously destroyed by the filter. Again this phenomenon indicates the reverse vesicles formed spontaneously, just like the case of the spontaneously formation of normal vesicles of cationic and anionic surfactants in dilute aqueous solutions. A typical micrograph of reverse vesicles formed in toluene after passing through a 0.22-μm filter was shown in Figure 3.

Unstable Reverse Vesicle Phase and Phase Transition in *n*-Heptane and *n*-Octane. Unlike the spontaneous formation of reverse vesicles in benzene, toluene, *tert*-butylbenzene, and cyclohexane, gentle shaking was usually necessary to get homogeneous bluish reverse vesicle phases in *n*-heptane and *n*-octane. The so-obtained reverse vesicle phases were found to be unstable. Up to a long time in storage, macroscopic phase separation would be observed from the top for these bluish reverse vesicle phases. Finally the upper phase became transparent and clear coexisting with a white opaque bottom phase. The formation of reverse vesicles in *n*-heptane and *n*-octane and the phase transition with time were found to be similar with those

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reported in the literatures typically formed by nonionic surfactants in liquid hydrocarbons, which were usually constructed by handshaking a two-phase system containing liquid crystals and excess oil and often rebounded to the initial state if kept for a period of time. These reverse vesicle phases also showed instability against centrifugation. Figure 4 shows the variation of phase behavior for a typical sample in *n*-heptane as a function of storage time and centrifugation.

If stored at room temperature for enough time for phase equilibrium, the bottom surfactant-rich phase would form a gel-like phase, which could not flow if induced only by its own gravity (inset of Figure 5). These gel-like phases could form not only for the reverse vesicle phases but also for the phases with ρ values slightly higher than those within which reverse vesicles formed. It should be pointed out that similar gel-like phases were also observed in cyclohexane for the mixture of TTAL and LA with ρ values higher than 0.91. If stored at higher temperature such as 40 °C, the formation of a gel-like phase would be greatly accelerated. Under a polarized microscope, well-defined as well as deformed crosses could still be seen together with some bright strips. This indicated that the gel-like phase was not a simple condensed phase of reverse vesicles, although some of reverse vesicles were also included in it. SAXS measurements revealed a sharp peak located around 5.75 nm^{-1}. If this phase is taken as a reverse lamellar liquid crystal phase, its interlayer distance *d*, i.e., one surfactant bilayer plus an organic solvent layer, was calculated to be 1.1 nm according to the following equation

$$d = 2\pi/q_{max} \qquad (1)$$

This value, however, was difficult to be accepted because it was even smaller than the extended molecular length of a single surfactant molecule of TTAOH or LA. So the gel-like phase was probably a mesophase between a well-defined reverse liquid crystal phase and a solid crystal of surfactant. A typical polarized micrograph and SAXS result were given in Figure 5.

Phase Behavior of Reverse Vesicles Induced by Temperature. Similar to the reverse vesicles formed by nonionic surfactants reported in the literature,[15−29] the reverse vesicles formed by salt-free catanionic surfactant mixture of TTAL and LA were also very sensitive to temperature. Increasing temperature could make the ρ values within which reverse vesicles were constructed move to higher values and vice versa, as has been pointed out in our previous work for reverse vesicles formed in toluene/water mixtures.[14] This was because the change of temperature would greatly alter the total HLB value of salt-free catanionic surfactant mixture and more hydrophilic TTAL was needed when the temperature was increased. The sensitivity of reverse vesicles toward temperature change could also be observed during polarized microscopy observations. It was very common to find the gradual disappearance of reverse vesicles due to a local temperature rise at higher magnifications where a mirror was usually used to focus light. Figure 6 gives the details of phase behavior variation as a function of temperature from 25 to 40 °C for reverse vesicles formed in toluene, *tert*-butylbenzene, and cyclohexane. Photos of some typical samples obtained at 25 and 40 °C, respectively, were given in Figure 7. Investigation of phase behavior variation as a function of temperature for reverse vesicles in *n*-heptane only obtained meaningless results and for the increase of temperature accelerated phase separation of the samples.

In addition to temperature, the phase behavior of reverse vesicles was also influenced by the weight fraction of total surfactants and water, as has also been clarified in our previous work.[14] If the weight fraction of total surfactants or water was below a certain value for a sample with fixed ρ value at a fixed
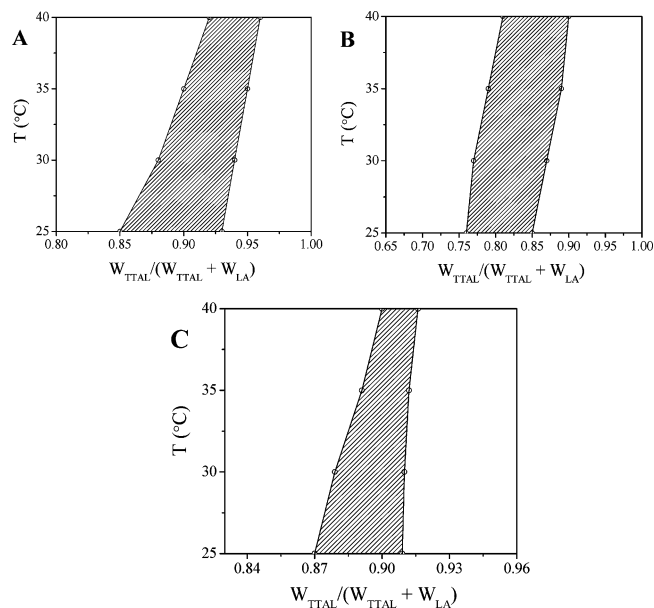

Figure 6. Temperature-induced phase transition of reverse vesicles formed in toluene (A), *tert*-butylbenzene (B), and cyclohexane (C), respectively. The shadowed region indicates reverse vesicles.

temperature, reverse vesicles could not form. This limited value, however, was usually very low. For example, the limited total surfactant content for a sample with $\rho = 0.90$ and volume ratio of H_2O to toluene being 1:4 was only found to be 0.004.[14] For a sample containing 0.05 g of total surfactants with $\rho = 0.90$ and 5 mL of toluene, the limited water content was found to be only 0.112 mL.[14] In other words, the composition of reverse vesicles formed by salt-free catanionic surfactant mixture TTAL/LA was adjustable in total surfactant weight and water content in a relative wide range once the weight fraction of TTAL to total surfactant and temperature was fixed.

Salt Resistance of Reverse Vesicles. It should be emphasized that one outstanding feature of reverse vesicles discussed in our experiments was that they formed by salt-free catanionic surfactant mixtures. By use of OH^- and H^+ as counterions of single-tailed cationic and anionic surfactants, respectively, their counterions will form water when mixed in equimolar ratio. If not so, it is impossible to construct reverse vesicles by traditional cationic and anionic surfactants because they are both hydrophilic and tend to exist as precipitates in organic solvents. So if salts were added to reverse vesicle phases formed by salt-free catanionic surfactant mixtures, it is well expected that they will be destroyed. This was proved by the fact that when we added $ZnCl_2$ or Na_2S to the reverse vesicles formed by TTAL/LA in a toluene/water mixture (the molar ratio of TTAL to $ZnCl_2$ or Na_2S was fixed to be 2:1), the blue reverse vesicle phases became transparently clear. However, by carefully lowering the amount of $ZnCl_2$ or Na_2S added to the reverse vesicle phases, reverse vesicles could not be destroyed, indicating they still had some salt resistance. Of course, this resistance was a function of the detailed composition of the tested reverse vesicle sample as well as the kind of salt added. In our experiments, we have successfully added ∼0.25 mL of 100 mmol·L^{-1} $ZnCl_2$ and Na_2S aqueous solution, respectively, to reverse vesicle phases of TTAL/LA formed in toluene (0.1 g total surfactants in 4.5 mL of toluene and 0.5 mL of water) without destruction of reverse vesicles. This opens the door to synthesize inorganic nanoparticles by using reverse vesicles as templates, and efforts toward this direction are currently under progress, and research results will be reported separately in near future.
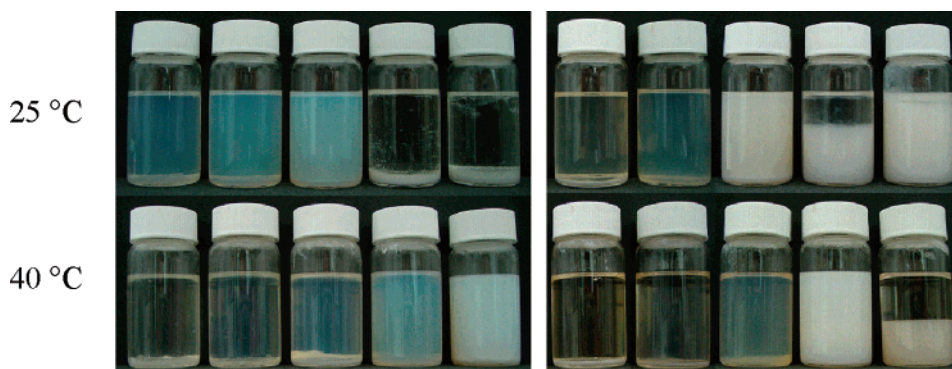
Figure 7. Phase behavior of reverse vesicles formed in *tert*-butylbenzene (left) and cyclohexane (right) at 25 °C (top row) and 40 °C (bottom row), respectively. Each sample contains 0.3 g of total surfactant, about 1.0 mL of H₂O, and 14 mL of *tert*-butylbenzene or cyclohexane, respectively. The weight fraction of TTAL on total surfactant are 0.77, 0.80, 0.83, 0.86, and 0.89 (from left to right) for reverse vesicles formed in *tert*-butylbenzene and 0.82, 0.88, 0.91, 0.94 and 0.97 (from left to right) for reverse vesicles formed in cyclohexane, respectively. The samples were allowed to equilibrate for two weeks at each temperature before taking photos.

Conclusions

A salt-free catanionic surfactant mixture of TTAL and LA could form reverse vesicles in selected organic solvents at the presence of a small amount of water. The reverse vesicles showed a blue color against sunlight and exhibited strong birefringence under a polarized microscope. In organic solvents including toluene, *tert*-butylbenzene, and cyclohexane, reverse vesicles formed spontaneously and were very stable, just like their counterparts, i.e., normal vesicles in aqueous solutions. In organic solvents including *n*-heptane and *n*-octane, reverse vesicles could still form but became unstable, and finally a gel-like phase usually formed at the bottom. In organic solvents, which were both good solvents for TTAL and LA, reverse vesicles could not form. The reverse vesicles formed by the mixture of TTAL and LA showed a strong dependence upon temperature change, which could be due to a disturbance of their total HLB value. An increase of temperature could make the ρ values within which reverse vesicles were constructed to move to higher values and vice versa. This feature was similar with that of reverse vesicles formed by nonionic surfactants in liquid hydrocarbons as reported in the literatures. Through suitable sample treatments, hydrophilic substances such as inorganic cations or anions could be trapped in the hydrophilic layers of reverse vesicles. This opens the door to prepare inorganic nanoparticles by using reverse vesicles as templates.

Supporting Information Available: More polarized micrographs of reverse vesicles formed in toluene, *tert*-butylbenzene, and cyclohexane. This information is available free of charge via the Internet at http://pubs.acs.org.

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