Reverse Vesicles of Salt-free Catanionic Surfactants in Toluene/Water Mixtures

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Stable reverse vesicles (RV) of salt-free catanionic surfactant system of tetradecyltrimethylammonium hydroxide (TTAOH) and lauric acid (LA) in toluene/water mixtures were prepared for the first time, which should broaden the potential applications of reverse vesicles.

Normal vesicles are uni- or multimolecular bilayers with hydrophobic parts inside and hydrophilic parts outside formed by lipids or surfactants in aqueous solutions. Reverse vesicles[1–4] are the counterparts of vesicles with hydrophilic parts inside and hydrophobic parts outside formed in nonaqueous solutions. Cationic and anionic (catanionic) surfactant mixtures are well known to form vesicles spontaneously in dilute aqueous solutions as described in 1989 by Kaler et al.[5] However, as their concentration increases, the excess salt formed by the counter ions can greatly screen the electrostatic interaction between aggregate films and leads to precipitate formation. In recent years, an increasing attention has been devoted to salt-free catanionic surfactant mixtures.[6–8] A typical way to eliminate the excess salt is by using OH^- and H^+ as counter ions of cationic and anionic surfactants, respectively, and by mixing them in equimolar ratio. The cationic surfactants used are usually alkyltrimethylammonium hydroxide, and the anionic surfactants are typically alkyl carboxylic acids. Although the aggregate formation of so-obtained salt-free catanionic surfactant mixtures in aqueous solutions has already been well studied,[6–8] their properties in nonaqueous solutions are rarely known. In this communication, we report for the first time the spontaneous reverse vesicle formation of a salt-free catanionic surfactant system of TTAL/LA/toluene, by adding a small amount of water.

To get zero-charged solid TTAL, which is equimolar mixture of TTAOH and LA, TTAOH stock solution was prepared firstly from aqueous TTABr (Merk) solution ($140\,\text{mmol}\cdot\text{L}^{-1}$) by strong base anion exchanger (Ion exchanger III, Merck) at 40 °C. The final concentration of TTAOH stock solution was determined by acid–base titration to be $122.1\,\text{mmol}\cdot\text{L}^{-1}$. To a known volume of TTAOH stock solution, equimolar solid LA (Shanghai Shiyi Chemicals Reagent Co., Ltd.) was added. After being kept at room temperature for several weeks during which frequent shaking was performed, LA dissolved completely, and the mixture was then dried below 40 °C to obtain solid TTAL. For phase behavior study, different amounts of solid TTAL and LA were weighed accurately to glass tubes before toluene or toluene/water was added, the tubes were then sealed and kept at room temperature for two months to reach phase equilibrium, and phase behavior was determined by visual observation and by a polarized microscope.

LA is soluble in toluene at room temperature, and its solubility is considerably high ($>0.6\,\text{g}\cdot\text{mL}^{-1}$). Like ionic surfactants, the solubility of zero-charged solid TTAL in toluene is rather low at room temperature but increases significantly when the temperature is above 35 °C. No reverse vesicles were found for all the samples of TTAL/LA/toluene at the absence of water at room temperature. In the LA rich region, a single clear, transparent phase was observed. With increasing weight fraction of TTAL on the total surfactant [$\rho = W_{\text{TTAL}}/(W_{\text{TTAL}} + W_{\text{LA}})$], insoluble substance was observed at the bottom of the tubes. After adding water to the samples to adjust the electrostatic interactions, reverse vesicles formed spontaneously for the samples with $0.84 \leq \rho \leq 0.92$. The reverse vesicular phases exhibited a bluish color against room light and the higher the ρ value, the heavier the bluish color. When $\rho < 0.84$, the bluish color became too weak to be distinguished. When ρ exceeded 0.90, however, a color change from bluish to yellowish was observed and finally when $\rho > 0.92$, the yellowish reverse vesicular phase became colorless. This color change was undoubtedly macroscopic reflection of variation of the number or size distribution of reverse vesicles induced by the different ρ values and gained further proof from polarized microscopic observations. We also found that the bluish vesicular solutions would become ultimately yellow if passed through a 0.22 µm pore size filter (Bedford, MA01730) to monitor the size distribution of the reverse vesicles.

The influence of amounts of added surfactant mixtures and water on reverse vesicle formation was examined. We fixed $\rho = 0.90$ and the volume ratio of H_2O to toluene being 1:4 and varied the amounts of added surfactants. No reverse vesicles were observed when the total surfactant weight ratio, $(W_{\text{TTAL}} + W_{\text{LA}})/(W_{\text{TTAL}} + W_{\text{LA}} + W_{\text{H}_2\text{O}} + W_{\text{toluene}})$, is lower than 0.004. We also varied the amount of added water to a sample containing 0.05 g of catanionic surfactant mixtures ($\rho = 0.90$) and 4.335 g of toluene (5 mL) and found that reverse vesicles could not form unless the amount of added water exceeded 0.112 g. At the bottom of the reverse vesicular phase a white phase formed which was assigned to be oil in water (O/W) emulsion. The volume of the emulsion was usually a bit larger than that of the added water. Photographs of three typical samples with different compositions are given in Figure 1.

Figure 2 shows photographs of the top reverse vesicular phases of typical samples with or without polarizers. Polydispersed reverse vesicles with diameters ranging from several hundred nanometers to tens of micrometers were clearly seen. This is consistent with the results reported by Nakamura et al. about the system of sucrose monoalkanoate/hexaethylene glycol hexadecyl ether/decane/water, where they claimed the size distribution of reverse vesicles produced by simple mixing is very large.[2b] From Figure 2 we can also see qualitatively that if the ρ value was changed, the averaged size of reverse vesicles would also be changed a lot.

The reverse vesicles were very sensitive to the temperature changes owing to the disturbance of the hydrophilic/lipophilic

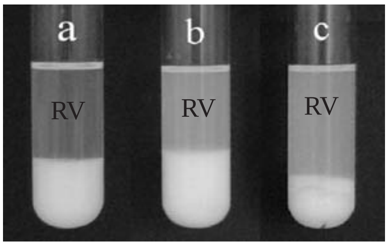

Figure 1. Three typical samples containing bluish reverse vesicular phases at the top and a white phase of oil in water (O/W) emulsion at the bottom. **a**) 0.172 g TTAL/0.028 g LA/2.5 g H_2O/2.5 g toluene ($\rho = 0.86$), **b**) 0.180 g TTAL/0.020 g LA/2.5 g H_2O/2.5 g toluene, ($\rho = 0.90$), and **c**) 0.180 g TTAL/0.020 g LA/1.2 g H_2O/3.8 g toluene ($\rho = 0.90$), respectively.

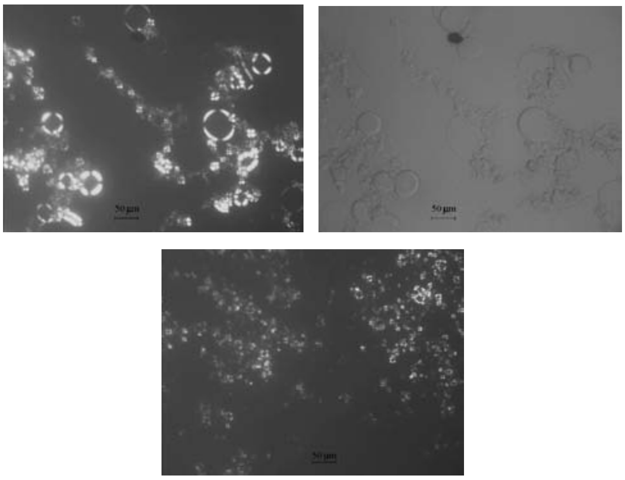

Figure 2. Typical micrographs of the reverse vesicular phases. Top row: sample **b** in Figure 1 with (left) and without (right) polarizers. Bottom: a sample with $\rho = 0.92$, the other conditions are the same with those of sample **b**.

balance values of the salt-free catanionic surfactant mixtures. Increasing temperature could make the range of ρ values of the formation of reverse vesicles move to higher values and vice versa. But if the temperature was above ≈50 °C, all the reverse vesicular phases would be destroyed and lost the bluish color, probably because at such temperatures both TTAL and LA became oil soluble and the surfactant molecules tended to exist as individuals rather than aggregates. To see if the reverse vesicles could also form in other organic solvents, we replaced toluene by benzene, cyclohexane, *n*-heptane, *n*-octanol, and tetrahydrofuran, respectively. The ρ value was fixed to be 0.90 and the volume ratio of H_2O to the organic solvent was fixed to be 1:4. Bluish reverse vesicular upper phase was observed only when benzene was the oil phase. In the case of cyclohexane, a highly turbid upper phase formed, which was probably water in oil (W/O) emulsion. For the other three solvents, only colorless, transparent phases were observed. However, we speculate that reverse vesicular phases may be constructed in some of these solvents if we further adjust the ρ value, the temperature and other conditions. Efforts toward this direction are currently under progress.

In summary, we successfully constructed reverse vesicles by using salt-free catanionic surfactant mixtures in nonaqueous solutions. To the best of our knowledge, this is the first time of constructing reverse vesicles by single-chained catanionic surfactant mixtures. The reverse vesicles formed by salt-free catanionic surfactant mixtures act similarly in some respects with those formed by nonionic surfactants such as they are highly polydispersed before extrusion, sensitive to the change of temperature and solvent. However, they also exhibit some characteristic features. For example, unlike the most reverse vesicular phases reported previously[1–4] 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, the reverse vesicles reported here formed spontaneously and were very stable at room temperature. This may open a new avenue to the investigation and application of reverse vesicles. Current results also remind us of the spontaneous vesicle formation of catanionic surfactant mixtures in dilute aqueous solutions.[5] It seems nature always has its symmetry not only of shape but also of process.

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