

## Two-Phase Region in the DTAB/SL Mixed Surfactant System

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The phase behavior as well as the microstructures of the dodecyltrimethylammonium bromide (DTAB)/sodium laurate (SL) aqueous two-phase system has been studied. By using FF-TEM, dynamic light scattering (DLS), a viscosity meter, and polarization microscopy, the effects of surfactant concentration and mixing ratio, temperature, salt concentration, and additives (octanol and toluene) on the phase separation have been systematically investigated. The phase separation is found to be strongly dependent on the variation of the surfactant aggregates. The different kinds of aqueous surfactant two-phase system can transit between each other upon the variation of the mixing ratio, the change of the salt concentration, and the addition of toluene and octanol.

### Introduction

Phase separation of the colloid system, a challenging problem in statistical mechanics, has attracted great attention in the past decade.<sup>1–12</sup> The liquid–liquid phase separation phenomenon is well established in the mixed polymer solution<sup>13,14</sup> and polymer–colloid mixtures,<sup>15,16</sup> called aqueous two-phase systems (ATPs), which are widely used for the extraction of the biomaterials.<sup>17–19</sup> In the “pure” surfactant solution, the phase separation phenomena were also observed. Correspondingly, the phase separation in the surfactant solution is termed as an aqueous surfactant two-phase system (ASTP). The cloud-point phenomenon, phase separation on heating, is well-known in the nonionic surfactant solutions.<sup>20–22</sup> In a few cases, phase separation was observed at the ionic surfactant systems.<sup>1,4,10–12</sup> Usually such ionic surfactants

have large and hydrophobic headgroups or the salt concentration was extremely high. In a recent paper, the fragile spongelike network was thought to resist miscibility with its own solvent and induce the coacervation at the zwitterionic gemini surfactant solution.<sup>2</sup> Under this situation, the phase separation is termed as “coacervation”, which is among the most esoteric in colloidal systems. Moreover, the cationic surfactant mixtures exhibit very interesting phase separation phenomena, which are induced by either the entanglement of rodlike micelles<sup>23</sup> or the formation of the lamellar phase.<sup>24</sup> Recently, in some cationic surfactant mixtures, we observed a new kind of liquid–liquid phase separation phenomenon:<sup>25</sup> both upper and bottom phases contain vesicles which packed densely and sparsely in the upper and bottom phases, respectively. In addition to the experimental studies on the phase separation of the surfactant solution, there is also some theoretical work.<sup>26–29</sup>

It is believed that the phase behavior of surfactant systems is determined by the surfactant aggregates as well as the interactions between them.<sup>30</sup> Our previous work has shown that the formation of an ASTP is strongly dependent on the surfactant aggregates. Up to now, there is no systematic work on the phase behavior of an ASTP, especially for the mechanism for its formation. To correlate the change of the macroscopic phase behavior with the transformation of the surfactant aggregates, it is hopeful to shed some light on the mechanism of the formation of the ASTP. By using FF-TEM, dynamic light scattering (DLS), viscosity, and polarization microscopy, we first systematically investigated the effects of surfactant concentration and mixing ratio, temperature, salt concentration, and additives (octanol and toluene) on the phase separation of the typical ASTP-forming system

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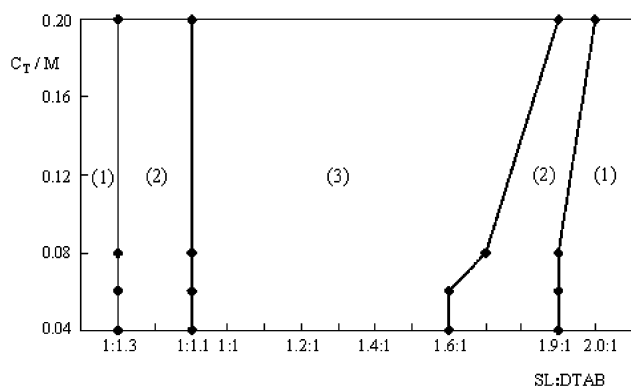
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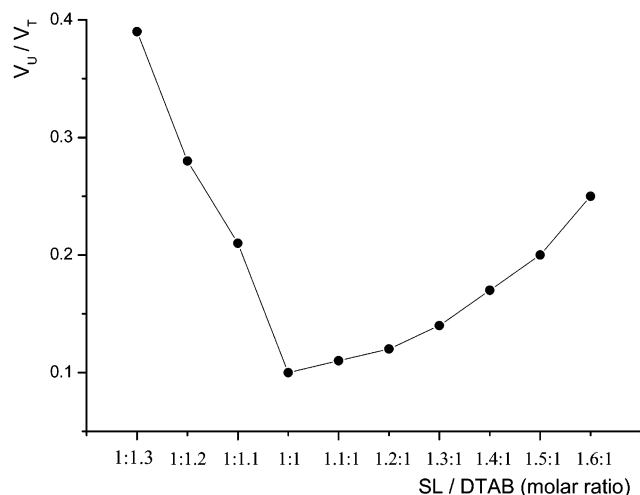
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**Figure 1.** Phase diagram for SL/DTAB ASTP ( $T = 30\text{ }^{\circ}\text{C}$ ): (1) isotropic single-phase; (2) ASTP without the birefringence phenomenon in the upper phase; (3) ASTP with the birefringence phenomenon observed in the upper phase.



**Figure 2.** Volume fraction of the upper phase in the SL/DTAB ASTP ( $T = 30\text{ }^{\circ}\text{C}$ ,  $C_T = 0.08\text{ M}$ ):  $V_U$ , volume of the upper phase;  $V_T$ , volume of total ASTP solution.

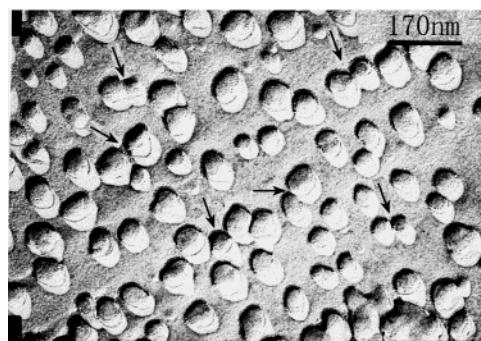
(sodium laurate/dodecyltrimethylammonium bromide mixed system).

## Experimental Section

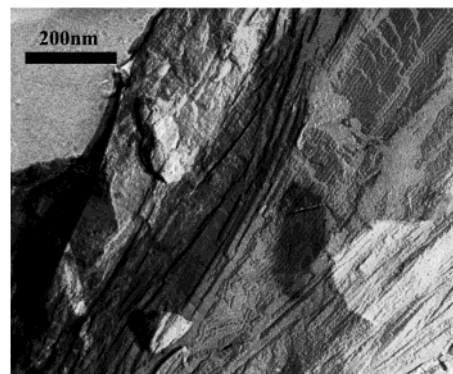
**A. Materials.** Sodium laurate (SL) was prepared by neutralizing lauric acid with NaOH in ethanol; then the solvent was removed and sodium alkylcarboxylates were dried. Lauric acid was the product recrystallized five times from 95% ethanol. Dodecyltrimethylammonium bromide (DTAB) was synthesized from dodecyl bromide and trimethylamine. Crude products were recrystallized five times from the mixed solvent of ethanol–acetone. The purity of all the surfactants was examined, and no surface tension minimum was found in the surface tension curve. NaBr was baked at  $600\text{ }^{\circ}\text{C}$  for 6 h before use. The water used was redistilled from potassium permanganate. The other reagents were products of Beijing Chemical Co., A. R. Grade.

**B. Methods. Sample Preparation.** Samples were prepared by mixing SL and DTAB at desired concentrations and mixing molar ratio. After sealing, samples were vortex mixed and then equilibrated in a thermostated bath controlled to a given temperature. The pH of the SL/DTAB mixed system was fixed to 9.2 ( $0.01\text{ M Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) to control the hydrolysis of SL. The formation of the ASTP would take several hours. All samples were equilibrated for at least one month before investigations.

**Electron Microscopy.** Samples for electron microscopy were prepared by freeze–fracture replication according to standard techniques. Fracturing and replication were carried out in a high vacuum freeze-etching system (Balzers BAF-400D). Replicas were examined in a JEM-100CX electron microscope.



**Figure 3.** FF-TEM micrograph of the upper phase in the DTAB/SL ASTP (SL/DTAB = 1:1.3,  $C_T = 0.08\text{ M}$ ,  $T = 30\text{ }^{\circ}\text{C}$ ). Vesicle–vesicle aggregation is clearly shown (see the arrows).



**Figure 4.** Lamellar structures observed by FF-TEM in the upper phase of the SL/DTAB ASTP ( $C_T = 0.08\text{ M}$ , SL/DTAB = 1:1.1,  $T = 30\text{ }^{\circ}\text{C}$ ).

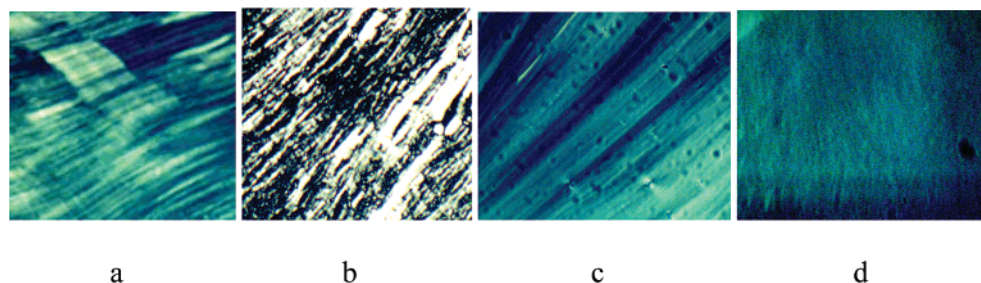
**Dynamic Light Scattering (DLS).** Dynamic light scattering measurements were made using a spectrometer of standard design (ALV-5000/E/WIN Multiple Tau Digital Correlator) and a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength). The scattering angle was  $90^{\circ}$ , and the intensity autocorrelation functions were analyzed using the methods of Cumulant and Contin. The solutions were centrifuged at a speed of 12000 rpm/min for 30 min to remove the dust before the experiment. The experimental temperature was controlled to  $30\text{ }^{\circ}\text{C}$ .

**Viscosity.** Viscosity was measured using an Oswald viscosity meter. The flowing time that fluid passed through the capillary was controlled to around 100 s so that the waste of kinetic energy could be neglected.

**Polarization Microscopy.** Photographs of birefringence were taken by polarization microscope (OLYMPUS BH-2) with Kodak-400 color films. The intensity of incident light as well as the time of exposure remained constant.

## Results and Discussion

**A. General Phase Behavior and the Microstructures.** The phase separation phenomenon was easily observed for the SL/DTAB mixed system when the mixing ratio was close to equimolar (from 1:1.3 to 2.3:1, mixing molar ratio of SL/DTAB) and the total concentration was larger than  $0.02\text{ M}$  (from  $0.02\text{ M}$  to  $0.2\text{ M}$  or higher). The formation of the ASTP in the catanionic mixtures seems to be reversible. If shaking the tube to mix the upper and bottom phases, the sample becomes a homogeneous clear solution. But several hours later the phase separation occurs again without any apparent change. If raising the temperature, the phase-separated sample becomes a clear homogeneous solution (discussed in the next part). Once the temperature goes back to the initial temperature, the phase separation occurs with the same macroscopic appearance.



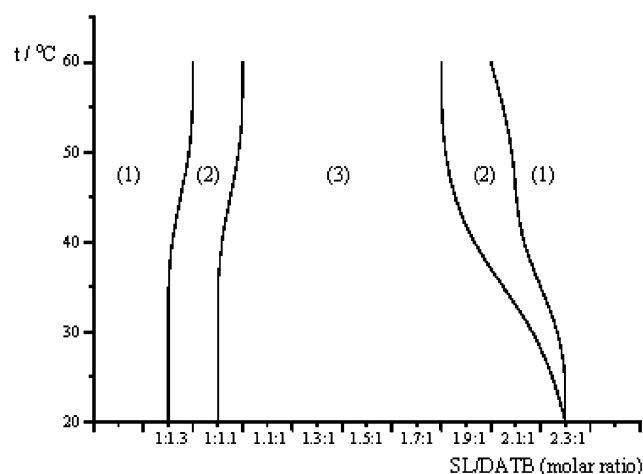
**Figure 5.** Photograph of upper phases of ASTP solutions ( $C_T = 0.08$  M,  $T = 30$  °C) through a polarization microscope: (a) 1:1.1; (b) 1:1; (c) 1.4:1; (d) 1.7:1 (SL/DTAB mixing ratio).

The anionic surfactant-rich side has a larger two-phase region than the cationic surfactant-rich side (Figure 1). The interface between the two phases is clear. The appearance of the upper phases is closely related to the mixing ratio. For instance, when the total concentration of the surfactant is fixed at 0.08 M (30 °C), the upper phase was transparent from 1:1.3 to 1:1.2 and from 1.7:1 to 2.3:1 but opalescent from 1:1.1 to 1.6:1. However, the bottom phases of the ASTP are always transparent in the experimental range investigated. The volume ratio of the upper and bottom phases is extremely sensitive to the mixing ratio. With the mixing ratio approaching 1:1, the volume fraction of the upper phase,  $V_U/V_T$  ( $V_U$ , volume of the upper phase;  $V_T$ , total volume of the ASTP solution), decreases and reaches the minimum where the mixing ratio is 1:1 (Figure 2). The volume fraction of the upper phases also slightly increases with the increase of the total surfactant concentration.

The type of the ASTP, classified according to the surfactant aggregates in it, is strongly dependent on the mixing ratio. When the total concentration is 0.08 M (30 °C), the phase separation begins at 1:1.3 (Figure 2). The upper phase at this ratio is not birefringent, indicating no typical  $L_\alpha$  texture formation. The densely packed vesicles were observed in the upper phase by FF-TEM (Figure 3). With the mixing ratio approaching equimolar, the upper phase shows the birefringence. Under a polarization microscope, colorful stripes are observed, indicating the formation of the lamellar structure, which is corroborated by the FF-TEM observation (Figure 4). These colorful stripes became more and more distinct as the mixing ratio approached equimolar (Figure 5), due to the growth of the lamellar structures. Hence, with the mixing ratio close to equimolar, the vesicles in the upper phases transform into the lamellar structure. A similar structural transition is also observed at other different total concentrations and temperatures. It is well documented that the transformation from vesicles to a lamellar structure can be attributed to the reduction of surface charge density of vesicles as the molar ratio of anionic and cationic surfactants approaches equimolar.<sup>31</sup>

**B. Effect of Temperature.** The phase behavior of the ASTP is very sensitive to temperature (Figure 6). Raising the temperature, the volume of the upper phase increases gradually and finally the interface between two phases disappears at a certain temperature. For the ASTP at molar ratio 1:1.3, the phase separation disappears at about 40 °C. The two-phase region decreases with the raising temperature: the range for the ASTP formation is from 1:1.3 to 2.3:1 at 30 °C whereas the range is from 1:1 to 1:8:1 at 60 °C.

The structure of surfactant aggregates as well as the interactions between them will change with raising

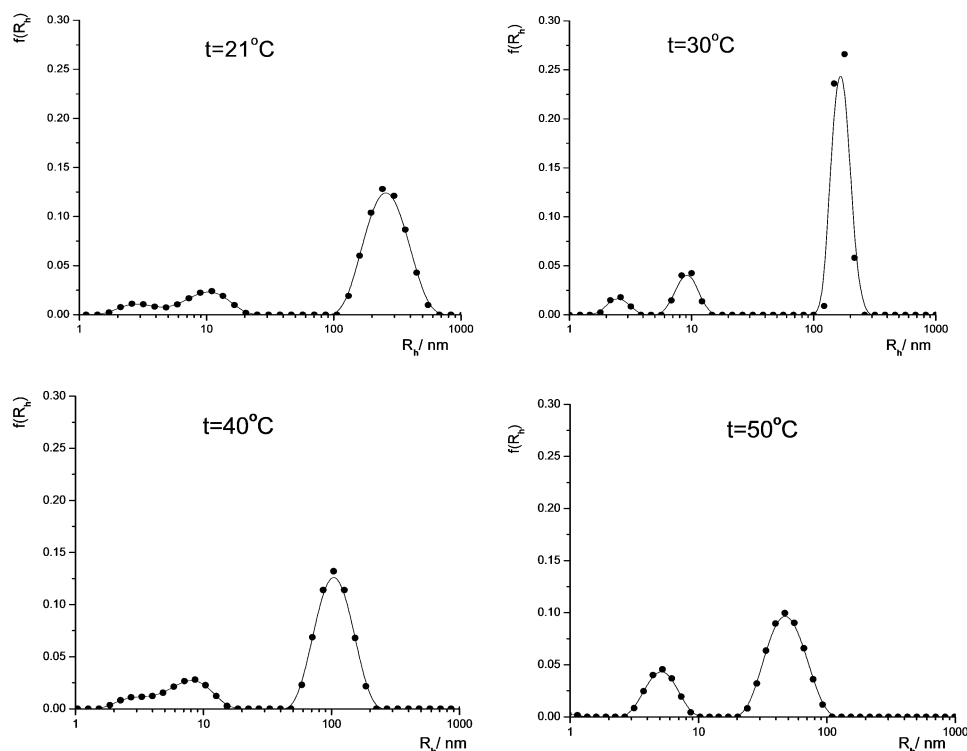


**Figure 6.** Effect of the temperature on the phase behavior of the SL/DTAB ASTP ( $C_T = 0.08$  M, pH = 9.2): (1) isotropic single phase; (2) two phases without the birefringence phenomenon in the upper phase; (3) two phases with the birefringence phenomenon observed in the upper phase.

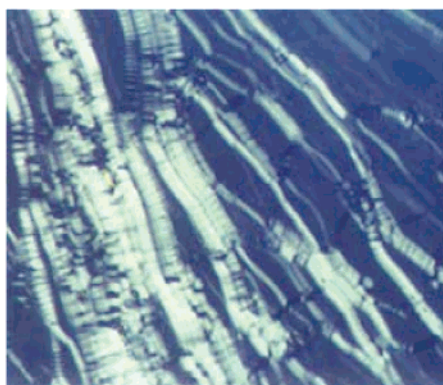
temperature. Structural transition of the surfactant aggregates in the upper phase of the SL/DTAB system ( $C_T = 0.08$  M, SL/DTAB = 1:1.3) is tracked by DLS. Figure 7 shows the variation of the hydrodynamic radius  $R_h$  distribution of the aggregates with raising temperature. At 21 °C the upper phase mainly contains two kinds of aggregates with the average sizes 258.7 and 6.9 nm, respectively. The size of the vesicles determined from DLS is obviously larger than that observed with FF-TEM. The size discrepancies of the vesicles between the results of TEM and DLS may be attributed to the aggregation of vesicles in the upper phases of the two systems (as shown in Figure 3). Since DLS would take the aggregated vesicles as a single particle, the equivalent hydrodynamic radius of vesicles from DLS would be much larger than what TEM would show. With the temperature rising to 30 and 40 °C, the average  $R_h$  of small aggregates does not change much whereas that of large aggregates decreases drastically. As the temperature reaches 50 °C, the average  $R_h$  of large aggregates is just 47.6 nm. Two possible reasons, the vesicles shrinking or the vesicles becoming less aggregated upon raising temperature, may contribute to the size decrease of the larger aggregates. Since the size of the vesicles at 50 °C is close to that determined from Figure 3 (30 °C), the latter seems more possible.

**C. Effect of the Electrolyte.** It is well-known that electrostatic interactions play an important role in modulating the phase behavior of catanionic surfactants.<sup>31</sup> Addition of salt generally tends to screen the electrostatic repulsion between aggregates and promotes larger aggregate formation. Upon the addition of NaBr, the transition from single-phase to ASTP is observed in the SL/DTAB mixed system.

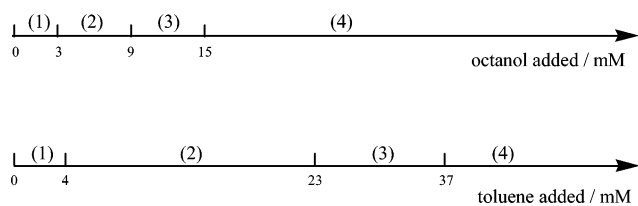
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**Figure 7.**  $R_h$  distribution of surfactant aggregates in the upper phase of the ASTP at different temperatures (SL/DTAB = 1:1.3,  $C_T = 0.08$  M).

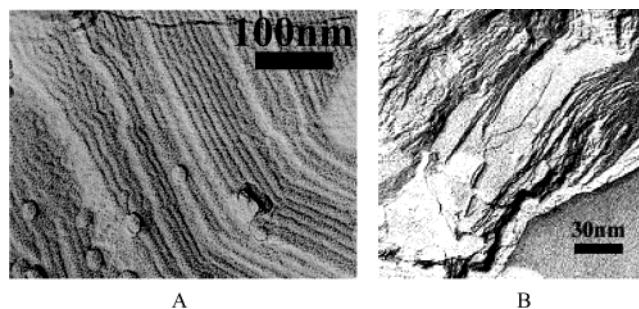


**Figure 8.** Polarization photograph of the lamellar liquid crystalline phase in the upper phase of the SL/DTAB ASTP with 0.5 M NaBr ( $C_T = 0.08$  M, SL/DTAB = 3:1,  $T = 30$  °C).



**Figure 9.** Phase behaviors of the SL/DTAB solution upon the addition of octanol and toluene ( $C_T = 0.08$  M, SL/DTAB = 1:1.4,  $T = 30$  °C): (1) single phase; (2) ASTP without the phenomenon of birefringence found in the upper phases; (3) ASTP with the phenomenon of birefringence observed in the upper phases; (4) turbid solution.

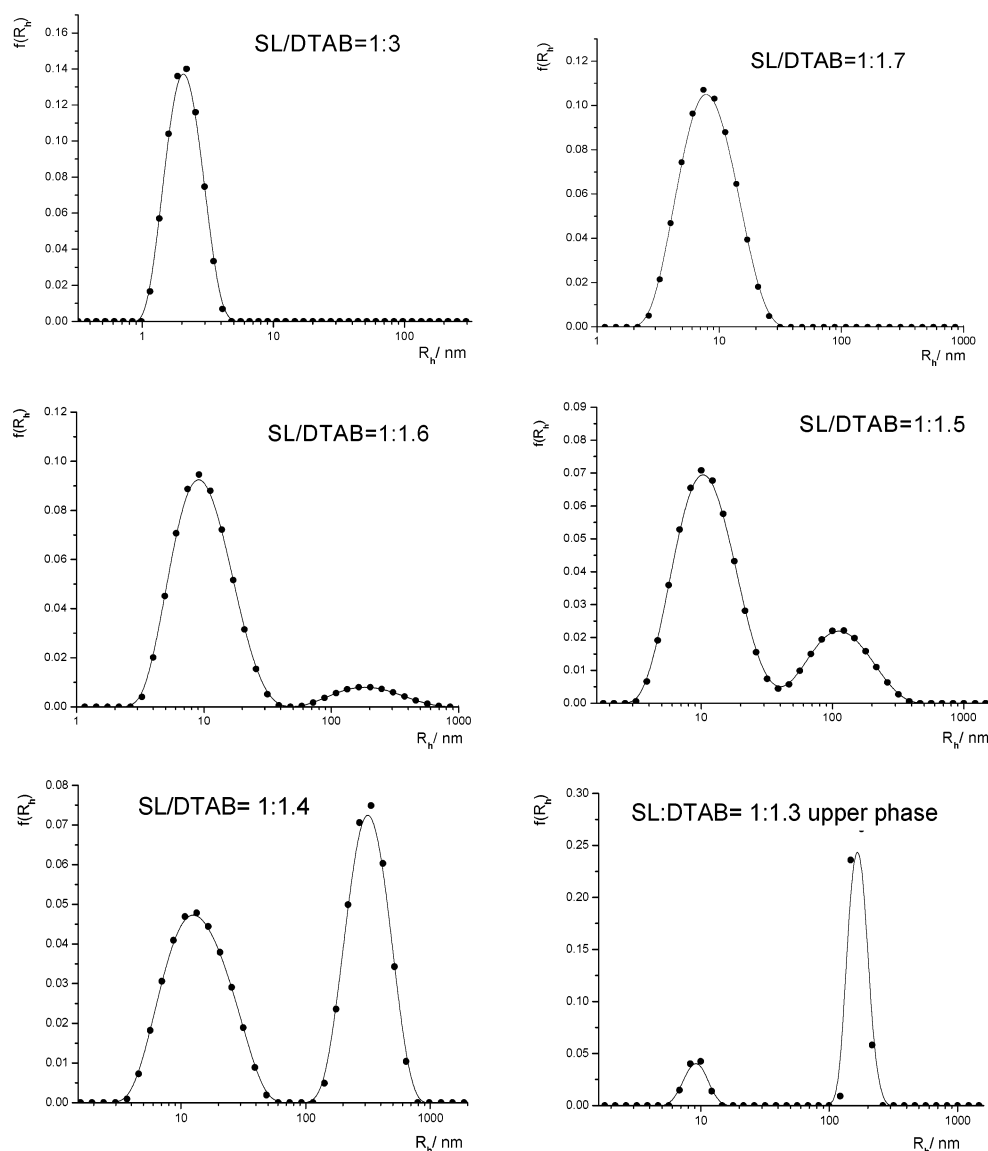
A micelle solution (SL/DTAB = 3:1,  $C_T = 0.08$  M) was used as the beginning of our research. From the result of DLS (Figure 11), the spherical micelles are the dominating aggregates in this solution. With the addition of salt, the viscosity shows a drastic change (Table 1), indicating the great change of the structure of the surfactant aggregates.



**Figure 10.** Lamellar structures in the upper phases of the ASTP by FF-TEM ( $C_T = 0.08$  M, SL/DTAB = 1:1.4,  $T = 30$  °C): (A) with 28 mM toluene; (B) with 12 mM octanol.

At low salt concentration (0.1 M), the viscosity of the system just increases slightly. With the salt concentration up to 0.2 M, the viscosity goes up dramatically, but the system still remains as a single phase. The formation of rodlike micelles probably accounts for the increase of viscosity. Further addition of NaBr (0.3 M) induces the phase separation, and the relative viscosity of the upper phase further increases. This phase separation may be induced by the entanglement of the rodlike micelles, similar to the case of the SOS/CTAB mixed system.<sup>23</sup> When the salt concentration reaches 0.5 M, birefringence is observed in the upper phase, indicating the formation of a lamellar structure (Figure 8). Thus, the transition between the two different kinds of ASTP is observed upon the change of salt concentration. In this system, the sequence of the phases upon the addition of salt is  $L_1$ ,  $L_1/L_1$ , and  $L_\alpha/L_1$ . Recently, a different sequence of phases was observed in the systems of CTAB/SHNC and CTAOH/HNC.<sup>32</sup> The transition from the micellar to the vesicle phase occurs for CTAOH/HNC over a two-phase region, where micelles and vesicles coexist. In the case of CTAB/

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**Figure 11.**  $R_h$  distribution of surfactant aggregates at different mixing ratios ( $C_T = 0.08$  M,  $T = 30$  °C) in the SL/DTAB mixed system.

**Table 1. Relative Viscosity of SL/DTAB Mixtures with Added NaBr ( $C_T = 0.08$  M, SL/DTAB = 3:1,  $T = 30$  °C)**

NaBr added (M)	solution appearance	$\eta_r$
0	isotropic single phase	1.12
0.1	isotropic single phase	2.30
0.2	isotropic single phase	22.4
0.3	ASTP without the birefringence found in the upper phase	35.8, <sup>a</sup> 1.02 <sup>b</sup>
0.5	ASTP with the birefringence observed in the upper phase	/

<sup>a</sup> Relative viscosity of the upper phase. <sup>b</sup> Relative viscosity of the bottom phase.

SHNC the transition from the micellar to the lamellar phase occurs over a three-phase region, where a surfactant-poor phase coexists with a lamellar and a coacervate phase. In conclusion, for the catanionic surfactant mixtures, the sequence of the phase change can be different from system to system with the variation of the environmental conditions, such as salt and surfactant mixing ratio.

**D. Effect of Aromatic Hydrocarbon and Long Chain Alcohol.** The transition from single-phase to ASTP is also observed upon the addition of aromatic hydrocarbon

and long chain alcohol (Figure 9). When 3 mM octanol and 4 mM toluene were added respectively, the original single-phase solution turned into a ASTP. With the concentrations of octanol and toluene reaching 9 and 23 mM, respectively, the upper phase of the ASTP is birefringent. The lamellar structure is clearly observed at Figure 10. Some vesicles still exist among the stacks of the bilayers, which is strong evidence for the transition from vesicles to lamellar structure. The transition from the vesicle to the lamellar structure upon the addition of toluene was also observed in the homogeneous vesicle solution.<sup>33</sup>

**E. Mechanism for the Formation of the ASTP.** We have shown that three kinds of phase separation can occur in the SL/DTAB mixed system. The entangled rodlike micelles, densely packed vesicles, and lamellar structure can separate from the solution to form a new phase. The sponge phase, which was characterized at some liquid-liquid phase separation, is not observed in this system. The entangled rodlike micelles also form a network structure so that it can induce the phase separation. A

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lamellar structure is the kind of aggregate with a very large dimension, and it is often found to separate as a new phase in many surfactant systems. However, it is difficult to understand the phase separation involving the vesicles. What controls the formation of ASTP containing vesicles? On the basis of the effect of the temperature on the phase behavior as well as the microstructures of the ASTP, some arguments are presented below.

In recent years, there has been a considerable interest in the phase separation of binary mixtures of hard spheres with a large size ratio. The physical origin of the phase separation in hard sphere mixtures is the osmotic depletion effect. In a colloidal suspension containing spheres of two different sizes, when two large spheres approach each other, the small spheres are expelled from the closing gap, leading to an uncompensated osmotic pressure difference between the gap and the outer surfaces. Thus, there is an attractive force between the large spheres due to the extra volume that becomes available to the small spheres, increasing the entropy of the system. Such entropy driven phase separation has been observed in the binary emulsions.

From Figure 7 we know that the SL/DTAB mixed systems contain two different aggregates with a large size ratio, the micelles and the vesicles. To reveal the relationship between the phase separation and the surfactant aggregates, we use the DLS to track the size change of the surfactant aggregates with the variation of the mixing ratio at the constant surfactant concentration (Figure 11). When the mixing ratio (1:3) deviates from equimolar greatly, the small spherical micelles are the main aggregates in the solution. With the mixing ratio close to equimolar, the small spherical micelles grow and the large aggregates (vesicles) begin to form at the mixing ratio 1:1.6. Further, close to equimolar, the number of vesicles increases and finally the phase separation occurs at the mixing ratio 1:1.3. The amount of the small aggregates also has been reduced greatly. The number ratio of the micelle to the vesicle is strongly dependent on the mixing

ratio, especially when closing the phase separation region. That is why the volume ratio of the upper and bottom phases is extremely sensitive to the mixing ratio.

When two vesicles approach each other, the micelles are expelled from the gap, leading to the attractive depletion interactions between vesicles. If there are enough vesicles in the solution, macroscopic phase separation would occur. Hence, the phase separation would occur only when the mixing ratio is close to equimolar. It can not only be attributed to the coincidence that all the cationic–anionic mixed systems which form vesicle-type ASTPs are micelle and vesicle mixtures. Maybe it is not appropriate to take vesicles as hard spheres, but it is true that the deformation of the vesicles enhances the attraction between the vesicles.<sup>34</sup>

### Conclusion

The change of the phase behavior and the structural transition of the surfactant aggregates in the phase-separated catanionic mixture (DTAB/SL) were systematically studied. Raising the temperature causes drastic shrinkage of the larger aggregates but has little effect on the smaller aggregates and finally destroys the phase separation. The addition of the salt transforms the small micelles into large aggregates (the rodlike micelles and lamellar structure) and leads to the phase separation. The solubilization of octanol and toluene into the homogeneous solution also induces the phase separation. The formation of the two aqueous phases containing vesicles is discussed on the basis of the phase separation of binary mixtures of hard spheres with a large size ratio.

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