Surface Properties and Aggregates in the Mixed Systems of Bolaamphiphiles and Their Oppositely Charged Conventional Surfactants

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Two transition points were observed in the surface tension curves of the mixed systems of cationic bolaamphiphile BPHTAB (biphenyl-4,4′-bis(oxyhexamethylenetrimethylammonium bromide)) and its oppositely charged conventional surfactants. Transmission electron microscopy, dynamic light scattering, and isothermal titration microcalorimetric experiments demonstrated that spherical vesicles or elongated aggregates formed at the lower surfactant concentration than the corresponding critical micelle concentration (cmc), which led to the existence of two transition points in surface tension curves. Addition of 10% formamide into the mixed system broke the vesicles and elongated aggregates and made the first breaking point disappear. The biphenyl group in the BPHTAB molecule and the appropriate attractive interaction between the cationic and anionic headgroups of the surfactants had a great influence on the ability of vesicle formation and determined whether the two transition points would exist in the surface tension curve.

Introduction

Bolaamphiphiles, molecules with two polar groups connected by one or two hydrophobic chains, are receiving increased attention as building blocks for structures such as membranes, fibers, tubes, and so on.[1−6] The aggregate morphologies of bolaamphiphiles are dependent on their headgroups[7−11] and the structure of the hydrophobic chains.[11−15] The surface properties of bolaamphiphiles are also investigated and many new phenomena are observed due to their reverse U-shape conformation in surface phase.[16−19] However, in contrast to many studies on organized assembly formation[20−23] and surface properties[24,25] in conventional catanionic surfactant systems, the corresponding research on mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants is rare.

There is one transition point in surface tension curve indicating micelle formation in common surfactant systems. However, in some systems, two transition points exist in the surface tension curve. This phenomenon usually can be observed in the following two series of mixed systems: one is the mixture of fluorocarbon and hydrocarbon surfactants,[26−29] and the other is the mixed system of polymer and conventional surfactants.[30,31] After Klevens and Raison's report[26] on the fluorocarbon and hydrocarbon mixed system, several other reports[27−29] prove that existence of the two transition points in this system is due to the mutual phobicity of the hydrocarbon and fluorocarbon chains. The hydrocarbon and fluorocarbon surfactants form respective micelles in different concentrations; as a result, two transition points in the surface tension curve are observed. In the case of polymer and surfactant system, the surfactant adsorption on the polymer is responsible for the first transition point. This binding occurs abruptly in a similar fashion as micelle formation.[30] The second transition point indicates the surfactant micelle formation as usual.

It is easy to find that in both series of the mixed systems mentioned above there is a great structure difference between the two components: hydrocarbon and fluorocarbon chains in the first series, polymers and small conventional surfactant molecules in the second series. We have reported that the two transition points in one surface tension curve can also be observed in the mixed system of a cationic bolaamphiphile (biphenyl-4,4′-bis(oxyhexamethylenetrimethylammonium bromide), BPHTAB) and sodium dodecyl sulfate (SDS).[32] It is interesting to note that there is no great structure difference between the two hydrocarbon compounds in this mixed system. In fact, strong electrostatic attractive interaction between the polar headgroups of BPHTAB and SDS exists. To make a further study on the relationship between molecule structure and molecule properties in this kind of system, in this paper, three bolaamphiphiles with biphenyl groups in the middle of their molecules are synthesized. They are mixed with their oppositely charged conventional surfactants. Combined the results in the mixed systems of bolaamphiphiles having monophenyl group and their oppositely charged conventional surfactants, we try to explore the course of the existence of the two transition points in our systems. On the basis of the results of transmission

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Mixed Systems of Bolaamphiphiles

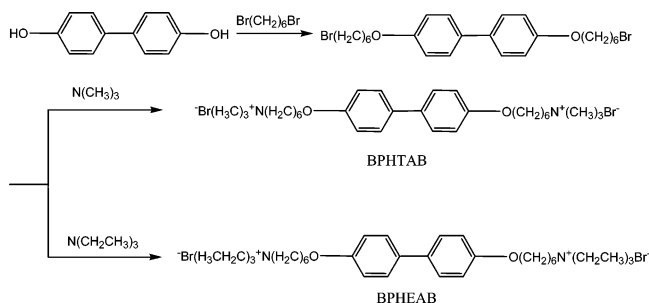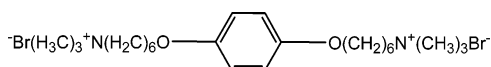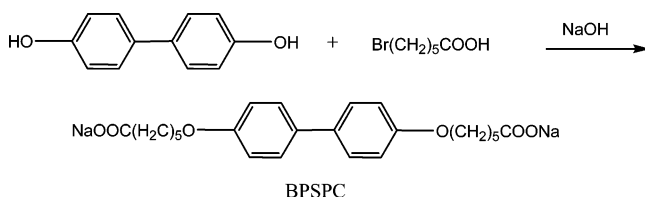*J. Phys. Chem. B, Vol. 108, No. 17, 2004* **5257**

SCHEME 1: Synthesis of BPHTAB and BPHEAB

CHART 1: Structural Formula of PHTAB

SCHEME 2: Synthesis of BPSPC

Figure 1. $\gamma - \log c$ curves of the BPHTAB/SDS mixed systems at 30.0 °C.

electron microscopy, dynamic light scattering and isothermal titration microcalorimetric experiments, we find that the formation of various kinds of organized assemblies such as vesicles or micelles at different surfactant concentrations will be responsible for the existence of two transition points in the surface tension curves.

Experimental Section

Materials. Biphenyl-4,4′-bis(oxyhexamethylenetrimethylammonium bromide) (BPHTAB) and biphenyl-4,4′-bis(oxyhexamethylenetriethylammonium bromide) (BPHEAB) were synthesized according to Scheme 1. First, 4,4′-bis((bromohexamethylene)oxy)biphenyl was synthesized by refluxing 4,4′-dihydroxybiphenyl, 1,6-dibromohexane, and K_2CO_3 in acetone for 3 days. The product was recrystallized from acetone. Second, BPHTAB and BPHEAB were obtained from 4,4′-bis((bromohexamethylene)oxy)biphenyl and the corresponding trialkylamine. The products were recrystallized from ethanol. Phenyl-4,4′-bis(oxyhexamethylenetrimethylammonium bromide) (PHTAB) (Chart 1) was prepared by the same procedure as BPHTAB except that hydroquinone was used instead of 4,4′-dihydroxybiphenyl. Biphenyl-4,4′-bis(sodium oxypentamethylenecarboxylate) (BPSPC) was synthesized from 4,4′-dihydroxybiphenyl and 6-bromohexoic acid in NaOH solution (Scheme 2). The product was recrystallized from an ethanol–water mixture. All the compounds were characterized by ^1H NMR spectra and elemental analysis.

Dodecyltrimethylammonium bromide ($C_{12}NMe_3Br$) and dodecyltriethylammonium bromide ($C_{12}NEt_3Br$) were synthesized from *n*-dodecyl bromide and the corresponding trialkylamine. The products were recrystallized from an ethanol–acetone mixture. Sodium decanoate (C_9COONa) was prepared by neutralizing the decanoic acid (C_9COOH) with NaOH in ethanol. C_9COOH was distilled twice before use. Sodium dodecyl sulfate (SDS) of AR grade was purchased from Sigma Co. and used as received. The purity of all the surfactants was examined by surface tension measurement, and no minimum was found in all the surface tension curves.

Ethanol was refluxed with magnesium scraps and iodine for more than 2 h and then distilled. Sodium bromide of AR grade
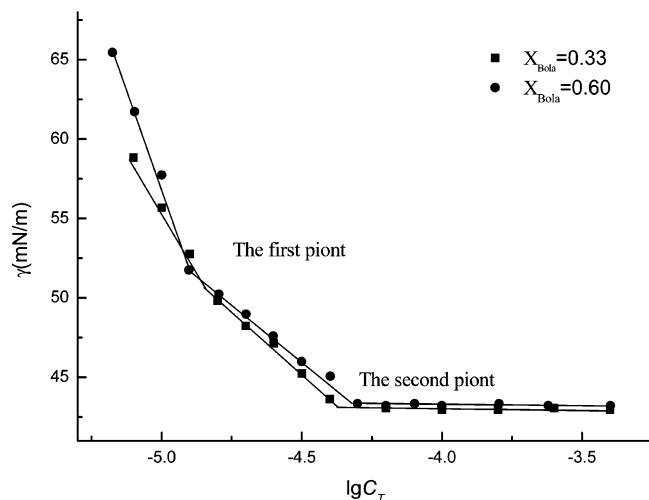
was baked at 500 °C for 6 h. Formamide (AR grade) and $Na_2B_4O_7\cdot10H_2O$ (AR grade) were from Beijing Chemical Co. and used as received. Water was distilled from the $KMnO_4$-containing deionized water to remove traces of organic compounds.

Sample Preparation. The surfactants were mixed in molar ratios and the solvents (ethanol/water and formamide/water) were mixed in volume ratios. X_{Bola} stood for the molar content of bolaamphiphile in the mixture. The pH values were adjusted to 9.2 by addition of $Na_2B_4O_7\cdot10H_2O$ in the systems containing carboxylate surfactants. The temperature of all experiments was kept at 30.0 ± 0.5 °C.

Surface Tension. The surface tension measurement was conducted using the drop volume method.[33] The values of concentration and the surface tension at the two transition points were determined from the surface tension curves ($\gamma - \log c$ curves).

Transmission Electron Microscopy (TEM). Micrographs were obtained with a JEM-100CX II transmission electron microscope by the freeze fracture technique and negative-staining methods. (1) Freeze-fracture technique: Fracturing and replication were carried out in an EE-FED.B freeze-fracture device equipped with a JEE-4X vacuum evaporator. (2) Negative-stained method: Uranyl acetate solution (1%) was used as the staining agent. One drop of the solution was placed onto a carbon Formvar-coated copper grid (230 mesh). Filter paper was employed to suck away the excess liquid.

Dynamic Light Scattering (DLS). Dynamic light scattering measurements were carried out by a spectrometer of standard design (ALV-5000/E/WIN Multiple Tau Digital Correlator) with a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed using the methods of Cumulant and Contin.

Isothermal Titration Microcalorimetry. The calorimetric measurements were performed with the commercial microcalorimetric-measuring channel of the 2277 TAM (Thermometric AB, Jarfalla, Sweden). Raw data curves were integrated using Digitam 4.1 software.

Results and Discussion

Surface Properties. The $\gamma - \log c$ curves of the BPHTAB/SDS mixed systems of two surfactant proportions are shown in Figure 1. There are two transition points in each $\gamma - \log c$ curve,
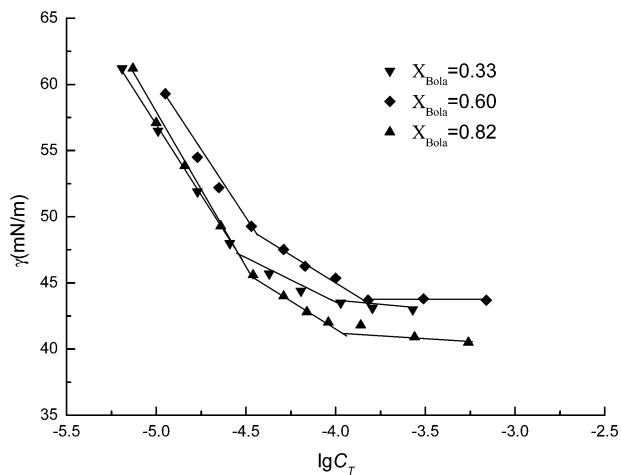
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Figure 2. γ−log c curves of the BPHTAB/SDS mixed systems in 0.1 mol/L NaBr at 30.0 °C.
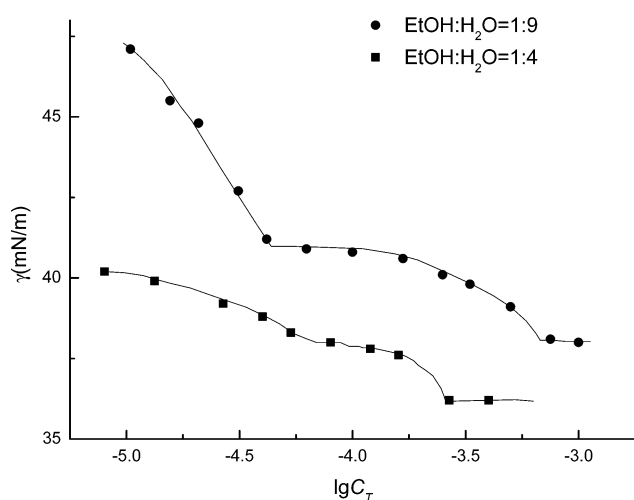

Figure 3. γ−log c curves of the BPHTAB/SDS mixed systems in 0.10 mol/L NaBr with ethanol addition at 30.0 °C ($X_{Bola} = 0.33$).

TABLE 1: C_1, C_2, γ_1, and γ_2 Values of the BPHTAB/SDS Mixed Systems at 30.0 °C

X_{Bola}	C_1 (10^{-5} mol/L)	C_2 (10^{-5} mol/L)	γ_1 (mN/m)	γ_2 (mN/m)
0.33	1.54	4.59	50.7	43.1
0.60	1.25	5.00	51.7	43.3

which is different from the case in the usual surfactant system. The transition point at lower concentrations is designated as the first point, and the transition point at higher concentration is designated as the second point (see Figure 1). The total surfactant concentrations at the two transition points (C_1, C_2) and surface tension values of the solution at the two transition points (γ_1, γ_2) are listed in Table 1.

The surface properties in the BPHTAB/SDS mixed systems in 0.10 mol/L NaBr were also investigated,[32] and the γ−log c curves are shown in Figure 2. It can be seen that the two transition points also exist, but the total surfactant concentration and surface tension at the transition point are different. Moreover, the two transition points also exist in the γ−log c curve with the addition of some ethanol (see Figure 3).

A similar result is also found in the BPHTAB/C$_9$COONa systems, especially when X_{Bola} is 0.60 and the pH is 9.2 (see Figure 4 and Table 2). In Figure 4, the two transition points are clearly shown in the γ−log c curve, and the concentration range between C_1 and C_2 is wider in the BPHTAB/C$_9$COONa system than that in the BPHTAB/SDS system. Meanwhile, the
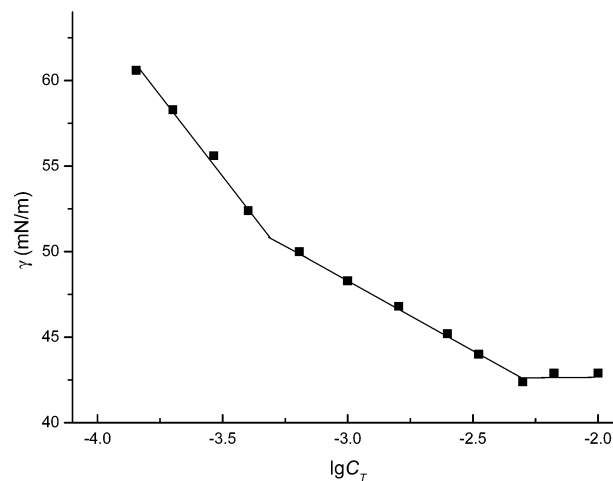

Figure 4. γ−log c curve of the BPHTAB/C$_9$COONa mixed systems at 30.0 °C ($X_{Bola} = 0.60$, pH = 9.2).

TABLE 2: C_1, C_2, γ_1, and γ_2 Values of the BPHTAB/C$_9$COONa Mixed Systems at 30.0 °C ($X_{Bola} = 0.60$, pH = 9.2)

X_{Bola}	C_1 (10^{-4} mol/L)	C_2 (10^{-3} mol/L)	γ_1 (mN/m)	γ_2 (mN/m)
0.60	4.47	5.00	50.9	42.6

values of C_1 and C_2 are higher in the BPHTAB/C$_9$COONa system than those in the BPHTAB/SDS system.

The above results indicate that it is not a unique phenomenon that the two transition points exist in one γ−log c curve in this bolaamphiphile and its opposite charged surfactant mixed system. Obviously the explanation for two transition points phenomenon in the fluorocarbon/hydrocarbon mixed surfactant systems and polymer/conventional mixed surfactant systems is not suitable for our systems. There is no mutual phobicity of the hydrocarbon and fluorocarbon chains or the surfactant's adsorption on the polymer. In fact, strong attractive interaction of cationic and anionic surfactants exists in the BPHTAB/SDS system and the BPHTAB/C$_9$COONa system. A new explanation for this new phenomenon should be provided.

Organized Assembly Formation. Organized assemblies are also studied in both the BPHTAB/SDS and BPHTAB/C$_9$COONa systems. TEM measurements show that spherical vesicles or elongated aggregates exist when the total surfactant concentration is higher than C_1 in the BPHTAB/SDS system (Figure 5a) and the BPHTAB/C$_9$COONa system (Figure 5b). Predictably, no aggregate is observed in the solution when the total surfactant concentration is lower than C_1 in these systems.

The DLS results of the BPHTAB/C$_9$COONa system in the total surfactant concentration of 0.002 mol/L (between C_1 and C_2) and 0.01 mol/L (above C_2) are shown in Figure 6. It can be seen that the aggregates with average hydrodynamic radius of 100 nm exist at 0.002 mol/L, which may be designated as vesicles and elongated aggregates. When the total surfactant concentration is increased to 0.01 mol/L, a new kind of aggregate with the average hydrodynamic radius of 2 and 17 nm can be observed, which usually indicates micelle formation. It should be noted that at this concentration vesicles (with the average hydrodynamic radius of 100 nm) still coexist in the system. TEM measurements also demonstrate that spherical vesicles or elongated aggregates exist at concentrations higher than C_2, in all the above systems. Combined with the TEM and DLS results, it can be concluded that vesicles and elongated aggregates exist while the total surfactant concentration is
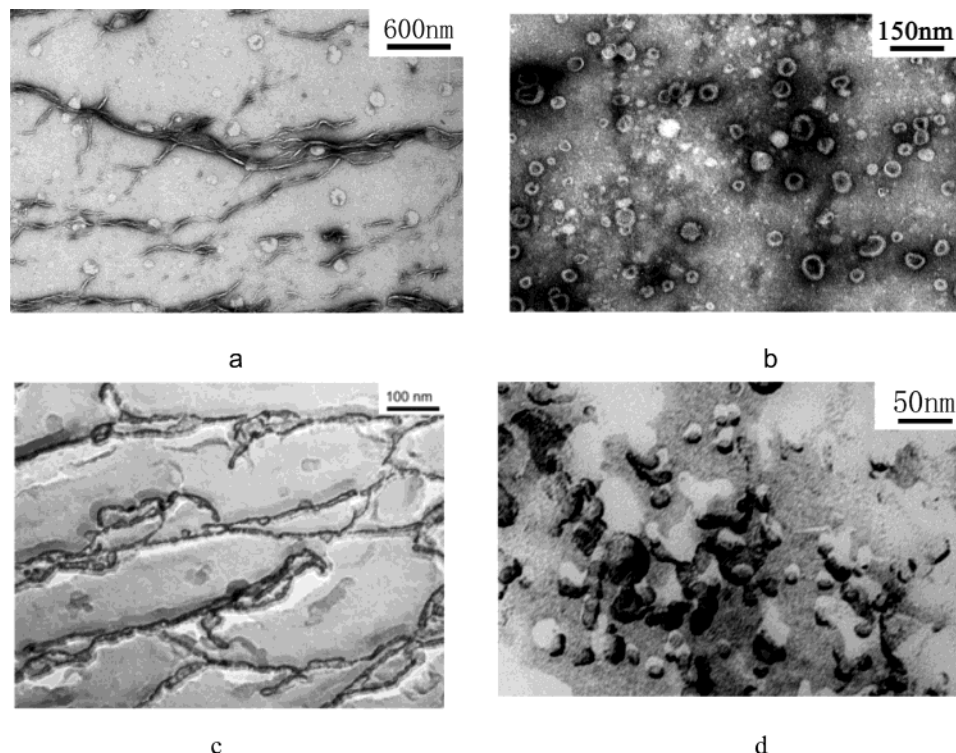
Figure 5. TEM micrographs for the mixed systems: (a) BPHTAB/SDS ($C_{total} = 3.0 \times 10^{-5}$ mol/L, $X_{Bola} = 0.60$, negative staining); (b) BPHTAB/C$_9$COONa ($C_{total} = 2.0 \times 10^{-3}$ mol/L, $X_{Bola} = 0.60$, pH = 9.2, negative staining); (c) BPHTAB/SDS ($C_{total} = 6.0 \times 10^{-5}$ mol/L, $X_{Bola} = 0.60$, 0.1 mol/L NaBr, freeze fracture); (d) BPHTAB/SDS ($C_{total} = 2.0 \times 10^{-4}$ mol/L, $X_{Bola} = 0.33$, EtOH:H$_2$O = 1:4, freeze fracture).
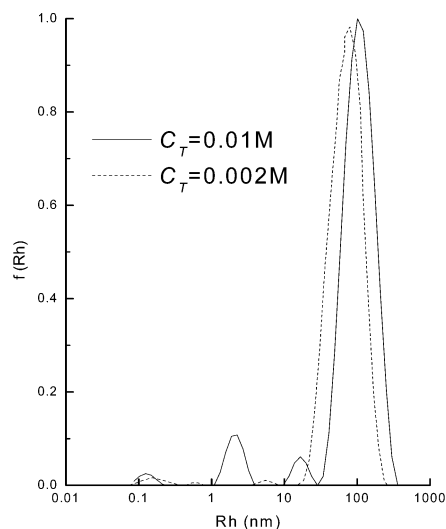

Figure 6. DLS measure results of the BPHTAB/C$_9$COONa system at 30.0 °C ($X_{Bola} = 0.60$, pH = 9.2).

between C_1 and C_2. When the concentration is above C_2, micelles begin to form and micelles and vesicles coexist in the solution.

It is well-known that the surface tension of surfactant solution is determined by the nature of surfactant molecules and their packing condition on the surface. Considering the equilibrium among surfactant molecules in surface, free surfactant molecules in the bulk phase and surfactant molecules in organized assemblies (such as micelles and vesicles), it is possible that the surface properties are influenced by the formation or transformation of the organized assemblies in the solution.

In usual surfactant system, there is no aggregate in the solution when the concentration is lower than the critical micelle concentration (cmc), so there is one transition point in the γ–log c curve indicating micelle formation. However, in the BPHTAB/

SDS and BPHTAB/C$_9$COONa systems, spherical vesicles and elongated aggregates form below the cmc, which influences the concentration of free surfactant molecule in the bulk solution, followed by the variation of the adsorption of surfactants. Thus it is reasonable that the existence of two transition points comes from the formation of different kinds of surfactant aggregates in different concentration regions. That is to say, the existence of two transition points is mainly due to the fact that spherical vesicle and elongated aggregate form at the lower surfactant concentration than the concentration of micelle formation. When the concentration is lower than C_1, no organized assemblies exist in the solution. Thus surface tension decreases with the increasing surfactant concentration according to the Gibbs adsorption equation. At the concentration of C_1, spherical vesicles or elongated aggregates begin to form, which influences the surface adsorption and induces the first transition point to appear. At the concentration of C_2, great amount of micelles begin to form, which induces the second transition point. That is to say, C_2 is the cmc in these kinds of systems.

Effect of Additives. The organized assemblies in these mixed systems with the addition of NaBr or ethanol are also investigated. TEM results show that spherical vesicles and elongated aggregates still exist when these additives are added into the system (Figure 5c,d). It is consistent with the results that vesicles can exist in 0.1 mol/L NaBr or at high volume ratio of ethanol/water solution in conventional cationic and anionic mixed surfactant systems.[34] Hence it is understandable that the two transition points phenomenon also exists in these systems after the addition of NaBr or ethanol, regardless of the variation of the total surfactant concentration and surface tension at the transition point.

However, it is completely different in the presence of formamide. The effect of formamide on the conventional cationic and anionic surfactants mixed system is different from that of ethanol based on our previous work.[35–38] According to
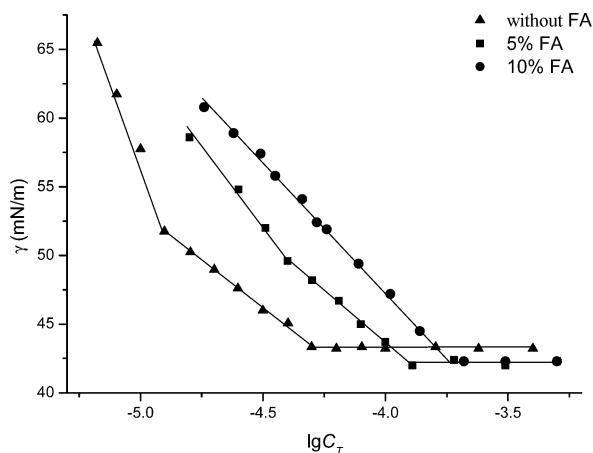
Figure 7. $\gamma-\log c$ curves of the BPHTAB/SDS mixed systems with and without formamide at 30.0 °C ($X_{Bola} = 0.60$).

TABLE 3: C_2 Values in the BPHTAB/SDS Mixed Systems with and without Formamide at 30.0 °C ($X_{Bola} = 0.60$)

formamide ratio (%)	$10^4 C_2$ (mol/L)
0	0.50
5	1.26
10	1.86

Coulomb's law, the relative dielectric constant of the solvent can directly affect the electrostatic force between two ionic surfactants. The dielectric constant of formamide is 111.0, which is much higher than that of water. The attractive interaction between the polar groups of cationic and anionic surfactants and the solvophobic effect would both be reduced with formamide addition. Therefore, formamide addition is disadvantageous to vesicle formation. On the other hand, surfactant micelles can exist in formamide solution according to Ray's work.[39] That is to say, if our explanation provided above is reasonable, we will observe the surface tension curve with just one transition point when formamide is added into the mixed systems in suitable concentration.

The $\gamma-\log c$ curves and the surface properties of the BPHTAB/SDS systems with and without formamide are shown in Figure 7 and Table 3, respectively. In Figure 7, the $\gamma-\log c$ curve of the system with 10% formamide is similar to the usual $\gamma-\log c$ curve, which has only one transition point. There are two transition points in the curve of the system with 5% formamide, but the first point is not obvious. TEM results demonstrate that neither the vesicle or elongated aggregate exists in the system with 10% formamide. For the system with 5% formamide, the density of vesicle or elongated aggregate is greatly reduced compared with that in the system without formamide addition.

The calorimetric measurement results also support the above conclusion. The isothermal titration microcalorimetric curves of the BPHTAB/SDS systems with and without10% FA addition are shown in Figure 8. From Figure 8a it can be found that there are two peaks in the curve of the BPHTAB/SDS system. The total surfactant concentrations of the two peaks are 1.78×10^{-5} and 5.08×10^{-5} mol/L, respectively. They are consistent with the total surfactant concentration at the two transition points in the $\gamma-\log c$ curve. Obviously, the first peak indicates the formation of vesicles and elongated aggregates ($\Delta H = -15.5$ kJ/mol), and the second peak indicates micelle formation ($\Delta H = -9.1$ kJ/mol). On the other hand, from Figure 8b it can be found that after the addition of 10% FA, there is only one abrupt decrease in the titration microcalorimetric curve, which indicates the micelle formation ($\Delta H = -10.9$ kJ/mol). Corresponding to
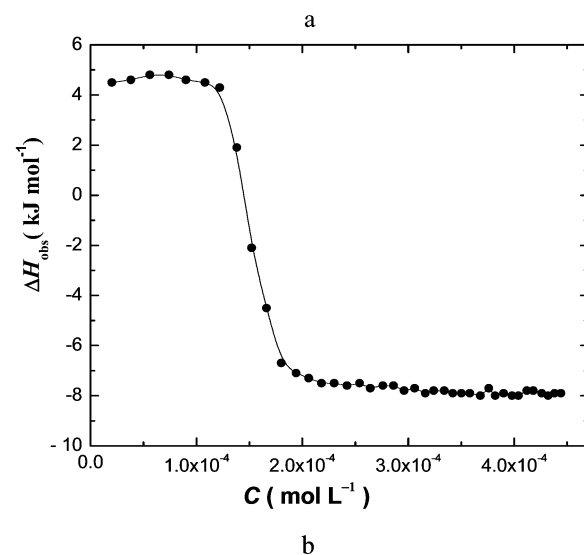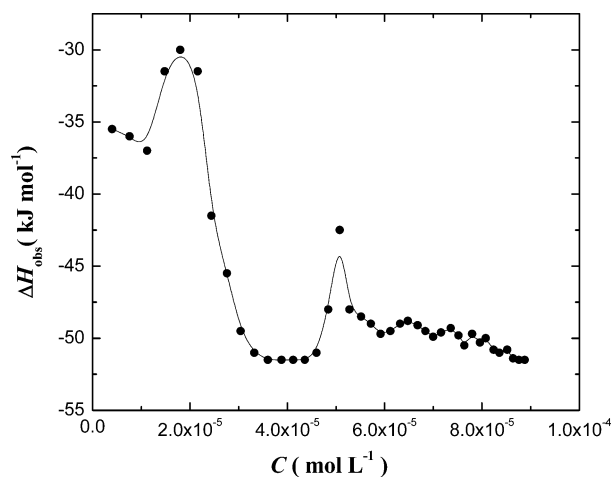

a

b

Figure 8. Titration microcalorimetric curves of the BPHTAB/SDS systems in water and in the 10% FA aqueous solution at 30 °C ($X_{Bola} = 0.60$): (a) without FA; (b) with 10% FA.

the value of the transition point of the $\gamma-\log c$ curve, the total surfactant concentration of the abrupt decrease in isothermal titration microcalorimetric curve is 1.52×10^{-4} mol/L.

Effect of Surfactant Molecular Structure. The phenomenon of the two transition points in the surface tension curve comes from the fact that the formation of spherical vesicles and elongated aggregates is prior to micelle formation. Usually in the conventional cationic and anionic surfactant mixed systems, vesicles form in the surfactant concentration near the cmc or higher than the cmc. Therefore, the phenomenon of two transition points is not common. Considering the fact that there is only one transition point in the surface tension curve in the PHTAB/SDS and PHTAB/C$_9$COONa systems,[19] we can assume that the biphenyl group in the BPHTAB molecule may play an important role in the priority formation of spherical vesicle and elongated aggregate.

Like other bolaamphiphiles, the BPHTAB molecule would take either of the two kinds of conformation in aggregates, line conformation, and U shape conformation. Neither of these conformations is in favor of micelles, as line conformation is not beneficial to the moving of BPHTAB molecules between micelle and solution (see Chart 2a), and the rigid biphenyl group is disadvantageous to the formation of U shape conformation in micelles (see Chart 2b). On the other hand, the line conformation of BPHTAB in the vesicles is more favored (see
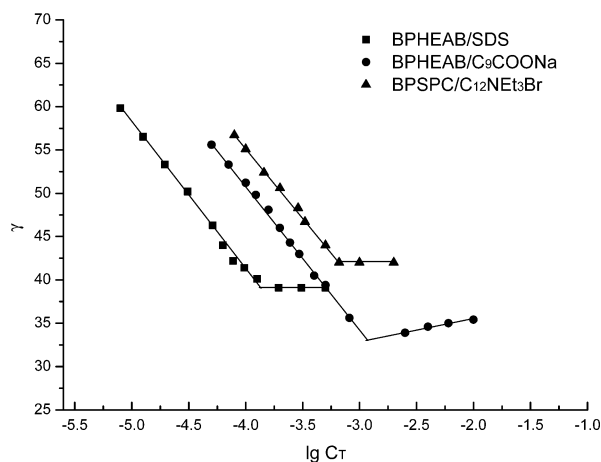
Figure 9. γ–log c curves of BPHEAB/SDS, BPHEAB/C$_9$COONa, and BPSPC/C$_{12}$NEt$_3$Br systems at 30 °C.

CHART 2: Conformation of BPHTAB Molecule in Aggregates: (a) Line Conformation of BPHTAB in the Micelle; (b) U Shape Conformation of BPHTAB in the Micelle; (c) Line Conformation of BPHTAB in the Vesicle
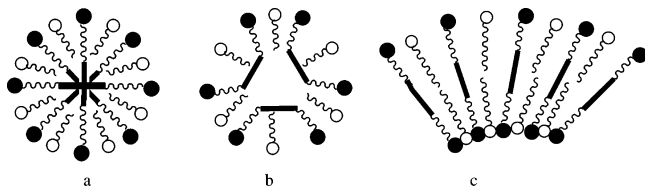

Chart 2c). Therefore, it is possible that spherical vesicle and elongated aggregate form at a lower concentration than the cmc.

However, the phenomenon of the two transition points occurs not in all the mixed systems of bolaamphiphiles with biphenyl group and their opposite charged conventional surfactants. Some other bolaamphiphiles with biphenyl groups, BPHEAB and BPSPC are synthesized in our lab. Due to the limited solubility of the BPSPC/C$_{12}$NMe$_3$Br system, only the BPHEAB/SDS, BPHEAB/C$_9$COONa, and BPSPC/C$_{12}$NEt$_3$Br systems are investigated. However, the surface tension curves of these three systems (see Figure 9) are similar to the usual case (only one transition point). Furthermore, vesicles are observed above the cmc and no vesicle or elongated aggregate is observed below the cmc according to the TEM results.

Obviously, there is another factor that influences the existence of the two transition points besides the effect of biphenyl group. The difference among these systems is polar headgroups of the surfactants. The headgroup effect on the aggregation behaviors could be explained by the critical molecular packing parameter P. According to the geometry rule,[40] P is calculated with the equation

$$P = V_c/a_0 l_c$$

where V_c and l_c are the volume and chain length of the hydrophobic group, respectively, and a_0 is the optimum area per polar group. For vesicle formation, the proper value of P falls in the range 0.5–1, whereas for micelle formation, $P < 0.5$. Considering that the triethyl group is bigger than the trimethyl group, the values of a_0 should be higher and P should be lower in the BPHEAB/SDS, BPHEAB/C$_9$COONa, and BPSPC/C$_{12}$NEt$_3$Br systems than those in the BPHTAB/SDS and BPHTAB/C$_9$COONa systems. Thus the vesicle-forming capability in the former three systems will be weak, and vesicles

cannot form at a concentration lower than the cmc. That is to say, bolaamphiphiles with a biphenyl group in the molecule and suitable interaction between polar groups in the mixed cationic and anionic surfactant system are the two basic determinants to the existence of the two transition points in one surface tension curve.

Conclusion

The surface properties and organized assemblies formation are studied in the mixed systems of bolaamphiphiles with biphenyl group and their oppositely charged conventional surfactants. Two transition points are observed in the surface tension curves of the BPHTAB/SDS and BPHTAB/C$_9$COONa mixed systems. Formation of different kinds of molecular assemblies in different concentration region accounts for this phenomenon, which is further explained by the structures of bolaamphiphiles. We hope that this study would make some advances in the field of the aggregate formation in the mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants, then provide some useful information on the relationship between surface properties and organized assembly formation in solutions.

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