

# Transitions of Organized Assemblies in Mixed Systems of Cationic Bolaamphiphile and Anionic Conventional Surfactants

Ting Lu, Feng Han, Zichen Li, and Jianbin Huang\*

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Honglan Fu

College of Life Science, Peking University, Beijing 100871, P. R. China

Received October 19, 2005. In Final Form: December 19, 2005

The transition from vesicles to tubelike structures has been studied in mixed systems of cationic bolaamphiphile BPHTAB [biphenyl-4,4'-bis(oxyhexamethylenetrimethylammonium bromide)] and its oppositely charged conventional surfactants with transmission electron microscopy (TEM) and dynamic light scattering (DLS). This transition can be attributed to the fact that tubelike structures are more stable aggregates than vesicles because of the special molecular packing in the aggregates of the mixed systems. The effects of temperature and salt addition on this transition have also been investigated, and the rate of the transition was found to be strongly dependent on temperature. Addition of the appropriate amount of NaBr will accelerate the transition from vesicles to tubelike structures, but the vesicles will transform into micelles at higher salt concentration. Moreover, the micelle-vesicle transition can be realized by addition of *n*-octanol in the mixed system of BPHTAB/sodium caprate (SC) at higher salt concentrations.

## 1. Introduction

Bolaamphiphiles are molecules with two hydrophilic heads connected by one or two hydrophobic chains.<sup>1</sup> In the past two decades, bolaamphiphiles have drawn much attention<sup>2–8</sup> for their many interesting properties. Usually, bolaamphiphiles can form monolayer membranes instead of bilayer membranes.<sup>9,10</sup> Kunitake et al. first reported the formation of aqueous monomolecular membranes from bola-form amphiphiles.<sup>11</sup> Because of their superior capability in forming monolayer membranes<sup>12</sup> and their superior vesicle stability at high temperature (> 80 °C),<sup>13</sup> vesicles facilitate the practical implementation of bolaamphiphiles as biomembrane models, drug-delivery systems, and microreactors. Moreover, tubelike vesicles<sup>14</sup> and fibrous<sup>15</sup> and helical<sup>16</sup> structures have been found in some kinds of bolaamphiphile systems. In 1993, Fuhrhop et al. prepared a monolayer tubular structure with

a bola-type surfactant with a diameter and length of 50 and 1000 nm, respectively.<sup>14</sup> Bhattacharya and Acharya<sup>17</sup> also prepared tubular structures in sugar-linked amphiphile systems. However, compared to the numerous works on single systems of bola-amphiphiles, reports on mixed systems of bola-form molecules and oppositely charged conventional surfactants are few,<sup>8</sup> and so far, work on transitions between organized assemblies in these mixed systems is rare.

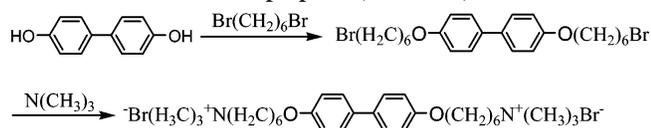
Research on structural transitions between various organized molecular assemblies is of great importance in both fundamental investigations and applications. Most such works have involved the addition of additives<sup>18,19</sup> or variation of environmental factors, such as temperature,<sup>20,21</sup> concentration,<sup>22,23</sup> and pH.<sup>24,25</sup> Some transitions have also been accomplished by the action of external forces such as shear<sup>26</sup> and agitation.<sup>27</sup> However, most work has concentrated on micelle-vesicle transformations, and research on the transition from vesicles to tubelike structures is still rare.<sup>28</sup> Recently, the application of bolaamphiphiles in the synthesis of mesoporous materials also attracted the attention of some researchers,<sup>29–31</sup> so it is necessary to systematically study the

\* To whom correspondence should be addressed. E-mail: jbhuan@pku.edu.cn.

- (1) Fuhrhop, J. H.; Mathieu, J. *Angew. Chem.* **1984**, *96*, 124.
- (2) Yiv, S.; Kale, K.; Lang, M.; Zana, R. *J. Phys. Chem. B* **1976**, *80*, 2651.
- (3) Fuhrhop, J. H.; Mathieu, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 100.
- (4) Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1937.
- (5) Kolbel, M.; Beyersdorff, T.; Sletvold, I.; Tschierske, C.; Kain, J.; Diele, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 1077.
- (6) Sirieix, J.; de Lauth, V. N.; Riviere, M.; Lattes, A. *New J. Chem.* **2000**, *24*, 1043.
- (7) Lu, Q.; Gong, H. F.; Liu, M. H. *Prog. Chem.* **2001**, *13*(3), 161.
- (8) Yan, Y.; Xiong, W.; Huang, J. B.; Li, Z. C.; Li, X. S.; Li, N. N.; Fu, H. *J. Phys. Chem. B* **2005**, *109*, 357.
- (9) Meglia, C. D.; Rananavare, S. B.; Svenson, S.; Thompson, D. H. *Langmuir* **2000**, *16*, 128.
- (10) Fuhrhop, J. H.; Fritsch, D. *Acc. Chem. Res.* **1986**, *19*, 130.
- (11) Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5231.
- (12) Mackenzie, K. C.; Bunton, C. A.; Nicoli, D. F.; Saelli, G. *J. Phys. Chem. B* **1987**, *91*, 5709.
- (13) Yan, Y.; Huang, J. B.; Li, Z. C.; Ma, J. M.; Fu, H. L. *J. Phys. Chem. B* **2003**, *107*, 1479.
- (14) Fuhrhop, J. H.; Spiroski, D.; Boettcher, C. *J. Am. Chem. Soc.* **1993**, *115*, 1600.
- (15) Franceschi, S.; Viguier, N. de; Riviere, M.; Lattes, A. *New J. Chem.* **1999**, *23*, 447.
- (16) Nakashima, N.; Asakuma, S.; Kim, J. M.; Kunitake, T. *Chem. Lett.* **1984**, 1709.

- (17) Bhattacharya, S.; Acharya, S. N. G. *Langmuir* **2000**, *16*, 87.
- (18) Walter, A.; Kuehl, G.; Barnes, K.; VarderWaerd, G. *Biochim. Biophys. Acta* **2000**, *1508*, 20.
- (19) Mao, M.; Huang, J. B.; Zhu, B. Y.; Ye, J. P. *Langmuir* **2002**, *18*, 3380.
- (20) Polozova, A. I.; Dubachev, G. B.; Simonova, T. N.; Barsukov, L. I. *FEBS Lett.* **1995**, *358*, 17.
- (21) Yin, H. Q.; Zhou, Z. K.; Huang, J. B.; Zheng, R.; Zhang, Y. Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 2188.
- (22) Maza, A. D. L.; Parra, J. L. *Colloids Surf. A: Physicochem. Eng. Aspects* **1997**, *127*, 125.
- (23) Zhai, L. M.; Zhang, J. Y.; Shi, Q. X.; Chen, W. J.; Zhao, M. *J. Colloid Interface Sci.* **2005**, *284*, 698.
- (24) Fukuda, H.; Goto, A.; Yoshioka, H.; Toto, R.; Morigaki, K.; Walde, P. *Langmuir* **2001**, *17*, 4223.
- (25) Johnsson, M.; Wagenaar, A.; Engberts, J. B. F. *N. J. Am. Chem. Soc.* **2003**, *125*(3), 757.
- (26) Mendes, E.; Menon, S. V. G. *Chem. Phys. Lett.* **1997**, *275*, 477.
- (27) Battersby, B. J.; Lawrie, G. A.; Barnes, G. T. *Colloids Surf. B: Biointerfaces* **1999**, *13*, 179.
- (28) Chen, W. J.; Zhai, L. M.; Li, G. Z.; Li, B. Q.; Xu, J. J. *Colloid Interface Sci.* **2004**, *278*, 447.
- (29) Behrens, P.; Glaue, A. M. *Monash. Chem.* **2002**, *133*(11), 1405.

**Scheme 1. Synthetic Routes for the Preparation of Bolaamphiphile (BPHTAB)**



regulation of the morphologies of the organized assemblies formed with bolaamphiphiles.

In this article, an interesting phenomenon, the transition from vesicles to tubelike structures, was observed as a function of time in several mixed systems of a bolaamphiphile with a biphenyl group and its oppositely charged conventional surfactants. The influences of temperature and salt were investigated for further understanding of this transition. The effect of the unique bolaamphiphilic molecular structure on this transition is also discussed.

## 2. Experimental Section

**Materials.** Sodium dodecyl sulfate (SDS, 99%) was obtained from Sigma Co. and used as received. Sodium caprate ( $C_{19}H_{37}COONa$ , abbreviated SC) was prepared by neutralizing the corresponding carboxylic acid with NaOH in ethanol ( $C_{19}H_{37}COOH$  was distilled twice to obtain pure products), then removing the solvents, and vacuum-drying the solid for 24 h. Bolaamphiphile BPHTAB [biphenyl-4,4'-bis(oxyhexamethylenetri-methylammonium bromide)] was synthesized as shown in Scheme 1 according to a previous report.<sup>32</sup>

**Sample Preparation.** The solutions of the mixed systems were prepared by simply mixing the single-surfactant stock solutions together. Samples were vortex mixed and equilibrated in a thermostatic bath at the appointed temperature before investigation. The mixing ratios are all molar ratio of the two components, and the  $\alpha_{\text{bola}}$  values refer to the molar fraction of bolaamphiphile in the mixed systems.  $C_T$  is the total concentration of surfactants in the system. The pH values were adjusted to 9.2 by addition of  $Na_2B_4O_7 \cdot 10H_2O$  in the systems containing carboxylate surfactants.

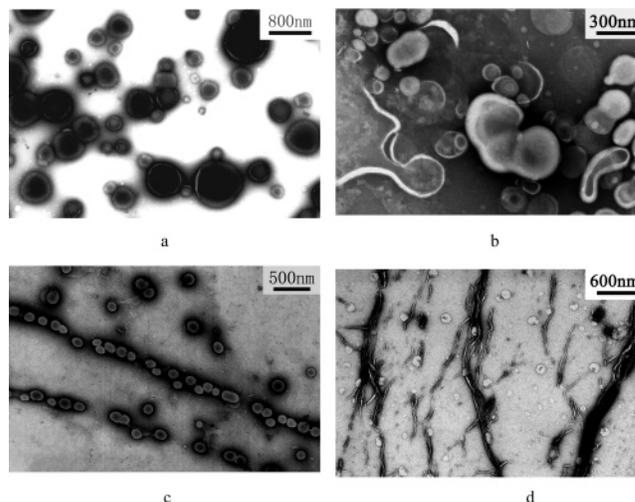
**Transmission Electron Microscopy (TEM).** TEM micrographs were obtained with a JEM-100CX II transmission electron microscope (working voltage of 80–100 kV) by the negative-staining method: Before being stained, the sample solution was adsorbed onto a copper grid by laying a carbon Formvar-coated copper grid (230-mesh) on one drop of the sample solution; the excess liquid was wiped away with filter paper. Then, one drop of the uranyl acetate solution (1%) as the staining agent was placed onto the copper grid. The excess liquid was also wiped away with filter paper. The process of adsorption was equilibrated in a thermostatic bath at the needed temperature.

**Dynamic Light Scattering (DLS).** Dynamic light scattering measurements were carried out using 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  $90^\circ$ , and the intensity autocorrelation functions were analyzed using the methods of Cumulant and Contin. The apparent hydrodynamic radius  $\langle R_h \rangle$  was deduced from the diffusion coefficient  $D$  by the Stokes–Einstein formula  $R_h = k_B T / (6\pi\eta D)$ . All measurements were made at  $30.0^\circ C$ .

(30) Bhaumik, A.; Samanta, S.; Mal, N. K. *Microporous Mesoporous Mater.* **2004**, *68*(1–3), 29.

(31) Shen, S. D.; Garcia-Bennett, A. E.; Liu, Z.; Lu, Q. Y.; Shi, Y. F.; Yan, Y.; Yu, C. Z.; Liu, W. C.; Cai, Y.; Terasaki, O.; Zhao, D. Y. *J. Am. Chem. Soc.* **2005**, *127*(18), 6780.

(32) Han, F.; He, X.; Huang, J. B.; Li, Z. C. *J. Phys. Chem. B* **2004**, *108*, 5256.



**Figure 1.** TEM micrographs for the mixed system of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$  mol/L) at  $22^\circ C$ : (a) within 3 days, (b) 3–7 days, (c,d) within the third week.

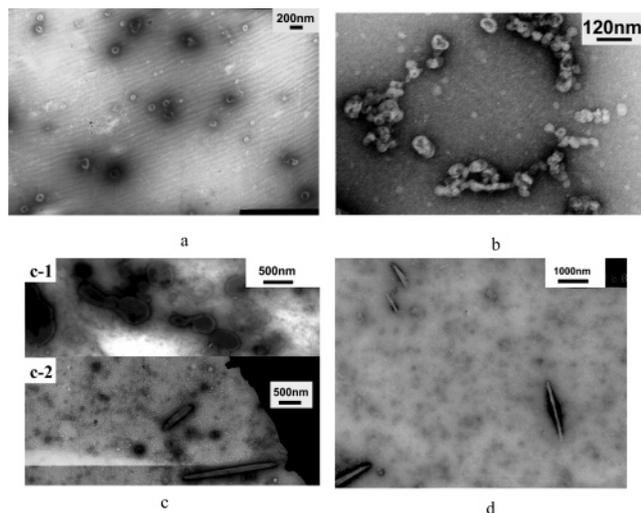
**Zeta Potential.** Zeta potentials were measured using a temperature-controlled ZetaPlus (Brook Heaven Co.) zeta potential analyzer.

## 3. Results and Discussion

**Vesicle Formation and Transition.** The mixed system of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$  mol/L) formed a clear and homogeneous solution at room temperature ( $\sim 22^\circ C$ ). TEM results revealed the formation of dispersed spherical vesicles with diameters of 200–800 nm in the system within 3 days (Figure 1a). Similarly to the other bolaamphiphiles, the BPHTAB molecules usually would take either of two types of conformations in aggregates, i.e., a line conformation or a U-shaped conformation. Considering the rigid biphenyl group in the BPHTAB molecule, the BPHTAB in the vesicles is more favored to take a line conformation than a U-shaped conformation.<sup>32</sup>

It is interesting to find that the morphology of the molecular assemblies in the system gradually changed with time, and a transition from vesicles to tubelike structures was observed by TEM (Figure 1). With increasing time, the vesicles aggregated together, and fusion between vesicles was also observed (Figure 1b). After the sample had been aged for 3 weeks, more vesicles were found to connect with each other, forming long tubelike structures with sectional widths of  $\sim 50$ – $80$  nm and lengths of  $\sim 1000$ – $2000$  nm (Figure 1c and d). Some of these elongated aggregates were branched and flexural. However, no obvious change in the appearance of the solution was observed in the transition process.

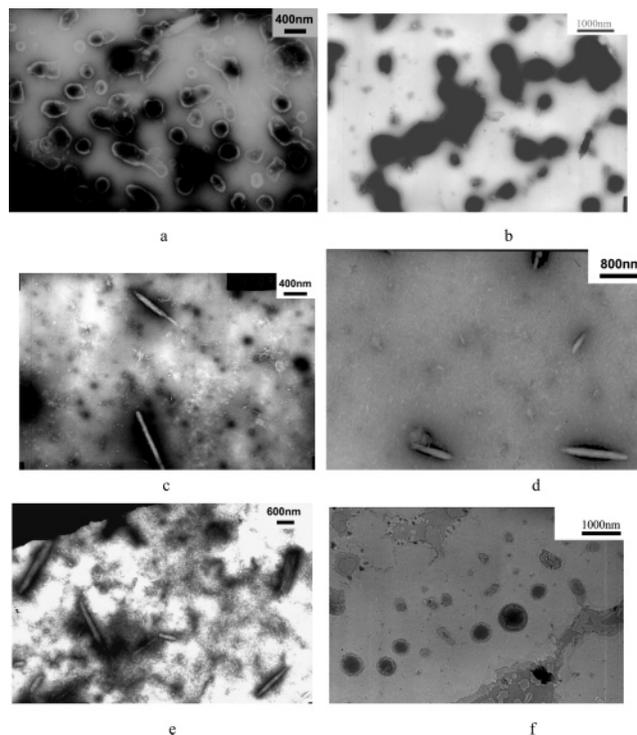
Similar results (Figure 2) were also found in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) at  $22^\circ C$ . Considering the fact that the critical micelle concentration for the mixed system of BPHTAB/SC is much greater ( $cmc = 5 \times 10^{-3}$  mol/L) than that of the BPHTAB/SDS mixed system ( $cmc = 5 \times 10^{-5}$  mol/L)<sup>32</sup> and that TEM observation of the mixed system of BPHTAB/SC is very difficult for dilute solutions, a total concentration of twice the  $cmc$  of the respective system was selected for investigation of the transformation of the organized assemblies. The dispersed spherical vesicles with diameters of 80–150 nm in the mixed system of BPHTAB/SC were found to aggregate and fuse with time, finally becoming transformed to tubelike structures with a diameter and length of about 100 and 1000 nm, respectively. Compared to those in the mixed system of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$



**Figure 2.** TEM micrographs for the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) at 22 °C: (a) 3, (b) 6, (c) 10, and (d) 12 days.

mol/L), the tubelike structures in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) had a larger ratio of diameter to length and were more like rigid rods.

It is well-known that vesicles are easily formed in catanionic surfactant systems.<sup>33</sup> Recently, our results also demonstrated that mixed systems of bolaamphiphiles and oppositely charged conventional surfactants also have strong vesicle-forming capabilities.<sup>8</sup> However, the length of a BPHTAB molecule is nearly twice the molecular length of SDS or SC (according to the results of Chem3D calculations, the molecular lengths of BPHTAB, SDS, and SC are 3.1, 1.7, and 1.3 nm, respectively). Combined with the characteristics of the BPHTAB molecule, which contains a rigid biphenyl group, we can assume that the molecules preferred to take a nearly parallel conformation in the membrane. Thus, from the view of energy, the molecules tended to arrange more closely in the assemblies, resulting in an increase of the critical packing parameter  $p$ , which is beneficial to the formation of larger assemblies such as tubelike structures ( $p$  is defined as  $v/a_0l_c$ , where  $v$  is the surfactant tail volume,  $l_c$  is the tail length, and  $a_0$  is the equilibrium area per molecule at the aggregate surface;  $0 \leq p \leq 1/3$  for spherical micelles,  $1/3 \leq p \leq 1/2$  for cylindrical micelles, and  $1/2 \leq p \leq 1$  for bilayer structures.<sup>34</sup>). On the other hand, closer molecular packing in the assemblies results in a decrease of the assembly curvature, which is also advantageous to the formation of bigger assembly. Thus, the vesicles have a tendency to lengthen in certain dimensions to decrease the curvature, which is more beneficial for forming tubelike structures than vesicles in these mixed systems considering molecular packing and the requirements of the curvature. Moreover, several factors affect the aggregation and fusion of vesicles such as the van der Waals force, hydration force, Coulombic force, and the fluidity of the membrane. The zeta potential values of the BPHTAB/SDS and BPHTAB/SC systems are +5 and +28 mV, respectively, at room temperature, which indicates that the electrostatic repulsion between aggregates is relatively weak.<sup>35</sup> Hence, from the viewpoint of kinetics, the



**Figure 3.** TEM micrographs for the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) at different temperatures and times: (a) 1, (b) 3, (c) 6, and (d) 8 days at 30 °C; (e) 1 day at 40 °C; (f) 50 days at 8 °C.

dispersed vesicles are easy to aggregate, following the occurrence of fusion between the organized assemblies. In fact, we assuredly observed the aggregation and fusion of the vesicles during the transition. Moreover, considering the facts that the molecular length of the SC molecule is slightly less than one-half that of BPHTAB molecule, it is reasonable that short rods instead of long tubes formed in the BPHTAB/SC system ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) because of the limitation of the membrane curvature.

**Temperature Effect.** The effect of temperature on the rate of transition from vesicles to tubelike structures in the BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) system was also investigated. It was found that temperature had a great influence on the rate of the transition from vesicles to tubelike structures. For example, the rate of the transition at 30 °C was obviously higher than that at 22 °C. Vesicle fusion and bunching and a transition to tubelike structures could be observed by TEM after 1, 3, and 6 days, respectively, at 30 °C (Figure 3a–d). This positive effect of temperature on the transition rate was sufficiently illustrated at 40 °C, where the rate of the transition was much higher and tubelike structures were found after 1 day (Figure 3e). In contrast, the transition rate was low at low temperature. Vesicles were still dispersed in the system after the sample had been aged for 50 days at 8 °C (Figure 3f). The corresponding results are summarized in Table 1, which clearly indicates that an increase in temperature can greatly accelerate the fusion of the vesicles, thus accelerating the whole process of the transition from vesicles to tubelike structures.

It is well-known that the Brownian motion of aggregates in solution is greatly influenced by the temperature. The diffusion rate of the molecules becomes higher with increasing temperature, which is helpful for the approach of the vesicles. Thus, the rate of transition from vesicles to tubelike structures would be accelerated at higher temperature. Further investigation showed that variation of the temperature can influence only the rate of

(33) Tondre, C.; Caillet, C. *Advances in Colloid and Interface Science* **2001**, *93*, 115.

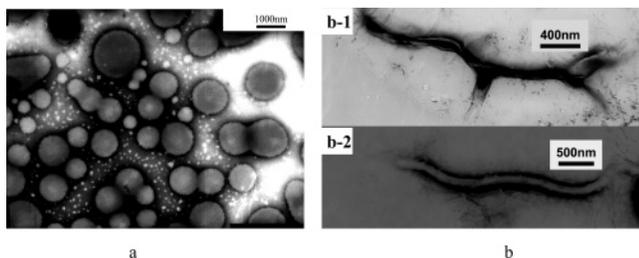
(34) (a) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525. (b) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *Biochim. Biophys. Acta* **1977**, *470*, 185. (c) Israelachvili, J. N.; Marcelja, S.; Horn, R. G. *Q. Rev. Biophys.* **1980**, *13*, 121.

(35) Kawasaki, H.; Imahayashi, R.; Tanaka, S.; Almgren, M. *J. Phys. Chem. B* **2003**, *107*, 8661.

**Table 1. Effect of Temperature on the Transition Rate in the System of BPHTAB/SC<sup>a</sup> as Determined by TEM<sup>b</sup>**

temp (°C)	1 day	3 days	6 days	10 days	50 days
8	a	a	a	a	a
22	a	a	c	d	
30	b	c	d		
40	d				

<sup>a</sup>  $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH = 9.2. <sup>b</sup> a, dispersed vesicles; b, fused vesicles; c, bunched vesicles; d, tubelike structures.



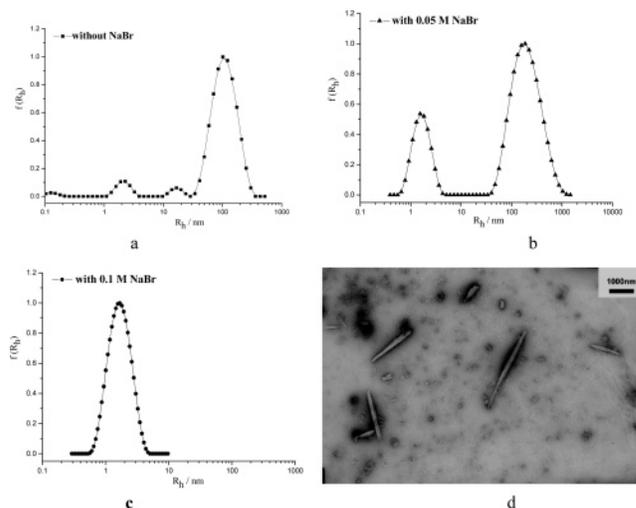
**Figure 4.** TEM micrographs for the mixed system of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$  mol/L, [NaBr] = 0.10 mol/L) at 22 °C: (a) 1 and (b) 10 days.

transformation from vesicles to tubelike structures but cannot transform the tubelike structures into vesicle as the temperature is decreased. For example, vesicles were still dispersed in the system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) when the sample had been aged for 50 days at 8 °C, but when the sample was aged at 40 °C, tubelike structures were found after only 1 day. Cooling the solution from 40 to 8 °C did not cause the tubelike structures to transform into vesicles. However, heating the solution from 8 to 40 °C again resulted in tubelike structures instead of vesicles being observed.

All of these results demonstrate that tubelike structures are more stable than vesicles in the range of experimental temperatures investigated. Variation of the temperature can influence only the rate of the transition from vesicles to tubelike structures.

**Salt Effect.** The effect of salt addition on the formation of aggregates and the rate of transition from vesicles to tubelike structures in the two mixed systems was also investigated. It was found that vesicles still existed in the mixed system of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$  mol/L) when the NaBr concentration reached 0.10 mol/L. However, the addition of NaBr greatly increased the rate of the transition from vesicles to tubelike structures. One day after the mixed system of BPHTAB/SDS with 0.10 mol/L NaBr addition had been prepared, fusion of the vesicles was clearly observed by TEM (Figure 4a). Tubelike structures formed after the solution had been equilibrated at 22 °C for 10 days (Figure 4b). A similar salt effect was also found in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2). When 0.05 mol/L NaBr was added, tubelike structures were observed by TEM in the fresh solution in the BPHTAB/SC system (Figure 5d). DLS results also showed two peaks with  $\langle R_h \rangle$  values of 2 and 190 nm, which are assigned to micelles and tubelike structures, respectively (Figure 5b). These results indicate that the addition of an appropriate amount of NaBr can accelerate the transition from vesicles to tubelike structures. This can be attributed to the fact that added salt will screen the repulsion between the aggregates of the mixed systems. Thus, the zeta potential is decreased, and the transition from vesicles to tubelike structures is also accelerated.

It was found that the variation of the mole fraction of BPHTAB ( $\alpha_{\text{bola}}$ ) greatly influenced the rate of the transition from vesicles to tubelike structures. In the mixed system of BPHTAB/SC ( $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2), the rate of the transition increased

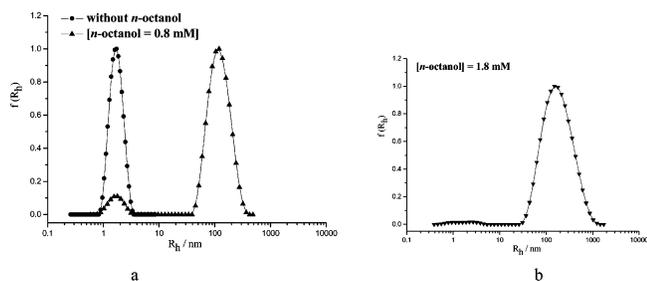


**Figure 5.** (a–c) Hydrodynamic radius ( $R_h$ ) distributions and (d) TEM micrograph of aggregates in the BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) mixed system: (a) without NaBr, (b) with [NaBr] = 0.05 mol/L, (c) with [NaBr] = 0.10 mol/L, and (d) freshly prepared with [NaBr] = 0.05 mol/L.

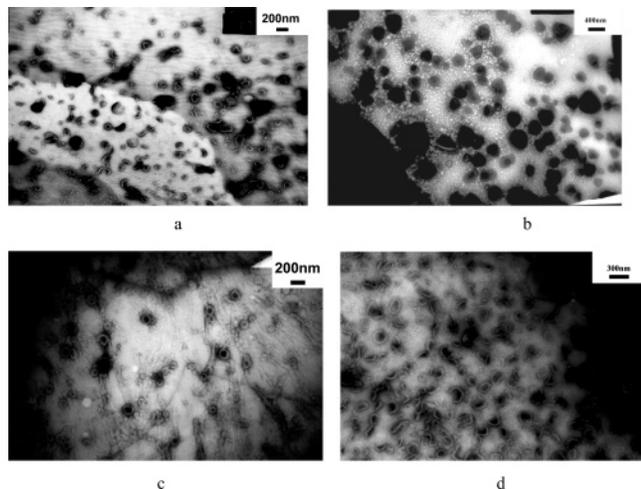
with increasing  $\alpha_{\text{bola}}$ . For example, for  $\alpha_{\text{bola}} = 0.8$ , tubelike structures were observed within 2 h after the solution had been prepared at 22 °C. On the other hand, when  $\alpha_{\text{bola}}$  was decreased from 0.60 to 0.46, the transition from vesicles to tubelike structures required more time. For example, at 40 °C, tubelike structures were observed after 48 h for the system with  $\alpha_{\text{bola}} = 0.46$ , compared to 24 h for the system with  $\alpha_{\text{bola}} = 0.60$ . However, when  $\alpha_{\text{bola}}$  was decreased to 0.05–0.14, only micelles were formed in the mixed systems because, in this case, the electrostatic interaction between the cationic and anionic surfactants was too weak. The above results further confirm our conclusion that the structure and mole fraction of the bolaamphile play an important role in the formation and transition of the organized assemblies in this kind of mixed system.

**Transition between Vesicles and Micelles upon Addition of NaBr and *n*-Octanol.** When 0.10 mol/L NaBr was added to the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2), the TEM results showed that no vesicles or tubelike structures existed in the system. DLS results also showed that the peak assigned to vesicles or tubelike structures with an average hydrodynamic radius,  $\langle R_h \rangle$ , of 110 nm completely disappeared, leaving solely the “micelle peak” with  $\langle R_h \rangle = 2$  nm (Figure 5a and c). Combined with the TEM results, it can be concluded that vesicles were destroyed and completely transformed into micelles in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) with 0.10 mol/L NaBr addition.

It is interesting to find that *n*-octanol addition can transform micelles to vesicles in the system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) with 0.10 mol/L NaBr. DLS results showed that the addition of 0.8 mM *n*-octanol made the original micelle peak with  $\langle R_h \rangle = 2$  nm shrink while another peak with  $\langle R_h \rangle = 120$  nm (Figures 5c and 6a) appeared. By TEM, spherical vesicles with a diameter of about 200 nm were observed (Figure 7a), which were approximately consistent with the newly appeared peak in the DLS plot. This transition continued upon further addition of *n*-octanol, and when 1.8 mM *n*-octanol had been added, the micelle peak almost disappeared, leaving only the vesicle peak with  $\langle R_h \rangle = 170$  nm (Figure 6b). Combined with the TEM results (Figure 7b), it can be concluded that the micelles were almost transformed into spherical vesicles. Thus, in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$



**Figure 6.** Hydrodynamic radius ( $R_h$ ) distributions of aggregates in the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L,  $[\text{NaBr}] = 0.10$  mol/L, pH 9.2) upon addition of  $n$ -octanol at 30.0 °C:  $[\textit{n}$ -octanol] = (a) 0.8 and (b) 1.8 mM.



**Figure 7.** TEM micrographs for the mixed system of BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L,  $[\text{NaBr}] = 0.10$  mol/L, pH 9.2) upon addition of  $n$ -octanol: (a)  $[\textit{n}$ -octanol] = 0.8 mM; (b)  $[\textit{n}$ -octanol] = 1.8 mM; (c)  $[\textit{n}$ -octanol] = 1.8 mM, room temperature for 5 months and 40 °C for 1 day; (d)  $[\textit{n}$ -octanol] = 4.5 mM.

mol/L, pH 9.2), the cycle of vesicles–micelles–vesicles could be realized by appropriate addition of NaBr and  $n$ -octanol. Furthermore, these vesicles existed for 5 months, and no transformation from vesicles to tubelike structures occurred during this period (Figure 7c), even when the solution was heated to 40 °C for 1 day. At increased  $n$ -octanol concentration, the vesicles still existed, and no tubelike structures were observed in the mixed system (Figure 7d).

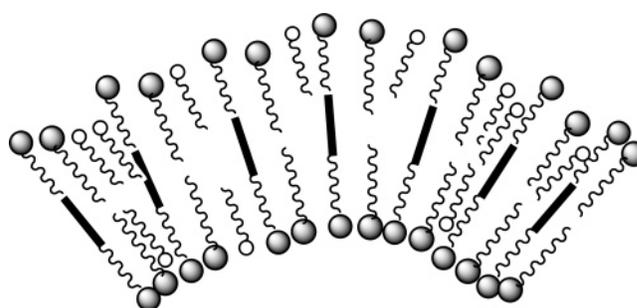
As is known, the addition of long-chain alcohols will decrease the curvature of surfactant aggregates; for example, the transition from wormlike micelles to vesicles has been observed under such conditions.<sup>36–38</sup> The addition of  $n$ -octanol can increase the effective hydrophobic chain volume ( $v$ ) of the surfactant molecules in the aggregates, thereby increasing the critical packing

(36) (a) Candau, S. J.; Zana, R. *J. Colloid Interface Sci.* **1981**, *84*, 206. (b) Hirsch E.; Candau S. J.; Zana R. *J. Colloid Interface Sci.* **1984**, *97*, 318.

(37) Chiruvolu, S.; Warriner, H. E.; Naranjo, E.; Idziak, S. H. J.; Rädler, J. O.; Plano, R. J.; Zasadzinski, J. A.; Safinya, C. R. *Science* **1994**, *266*, 1222.

(38) (a) Hoffmann, H.; Thunig, C.; Valiente, M. *Colloids Surf.* **1992**, *67*, 223. (b) Hoffmann, H.; Munkert, U.; Thunig, C.; Valiente, M. *J. Colloid Interface Sci.* **1994**, *163*, 217. (c) Gradzielski, M.; Bergmeier, M.; Müller, M.; Hoffmann, H. *J. Phys. Chem. B* **1997**, *101*, 1719.

**Chart 1. Conformations of Molecules in the Vesicle Membrane**



parameter  $p$  to satisfy the requirement for the formation of vesicles or even larger aggregates. On the other hand, the addition of  $n$ -octanol not only promotes the transition from micelles to vesicles, but also makes the vesicles show good stability with time, which is different from the vesicles in the previously studied systems. This can be attributed to the change in conformation of the molecular arrangement in the surfactant aggregates after  $n$ -octanol addition. Because of the relatively short length of the  $n$ -octanol molecule (0.9 nm according to results of a Chem3D calculation), the molecules in the membrane are no longer arranged in a parallel conformation but tend to bend and satisfy the curvature requirements of vesicles (Chart 1). Thus, it is reasonable that the vesicles exhibit good stability with aging time and do not transform into tubelike structures in this case.

#### 4. Conclusion

The transition from vesicles to tubelike structures was observed as a function of time in mixed systems of BPHTAB/SDS ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-4}$  mol/L) and BPHTAB/SC ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) without any addition of additives or agitation. That tubelike structures rather than vesicles are the more stable aggregate in these systems can be attributed to the structural characteristics of the surfactant molecules in the systems such as the bolaamphiphile's rigid biphenyl group and the suitable molecular length of the catanionic surfactants. Increasing the molar fraction of the bolaamphiphile was found to be beneficial for the transition from vesicles to tubelike structures. The rate of this transition can be controlled through the variation of the environmental temperature and the addition of NaBr. However, the addition of 0.10 mol/L NaBr to the BPHTAB/SC mixed system ( $\alpha_{\text{bola}} = 0.60$ ,  $C_T = 1 \times 10^{-2}$  mol/L, pH 9.2) transforms the vesicles into micelles, and subsequent  $n$ -octanol addition can realize the transition from micelles back into vesicles in this system. Vesicle composed of BPHTAB/SC/ $n$ -octanol are very stable, and no transformation from vesicles to tubelike structures occurred with the aging time. We anticipate that this work will make some advances in the field of self-assembly formation and transitions in mixed bolaamphiphile systems and might promote our understanding of adjusting surfactant self-assemblies and realize applications in related fields.

**Acknowledgment.** This work was supported by NSFC (20233010, 20373003, 20425310, 50521201) and the doctoral program of MOE in China.

LA0528100