



## Feature Article

## Recent advances in the mixed systems of bolaamphiphiles and oppositely charged conventional surfactants

Yun Yan, Ting Lu, Jianbin Huang\*

Beijing National Laboratory for Molecular Science (State Key Laboratory for Structural Chemistry of Unstable and Stable Species), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

## ARTICLE INFO

## Article history:

Received 31 December 2008

Accepted 27 April 2009

Available online 12 May 2009

## Keywords:

Bolaamphiphiles

Catanionic mixed systems

Surface property

Aggregation

Self-assembly

Vesicles

## ABSTRACT

Researches on the bolaamphiphiles have attracted considerable attentions in the last three decades. Among which, the mixed systems with conventional surfactants are of special interest. This review focuses on the recent advances in the research of the bolaamphiphile/oppositely charged conventional surfactant mixed systems. The following contents are covered: (1) surface properties, which include (i) the general properties of the mixed systems, (ii) the effect of rigid group on the surface properties, and (iii) the slow adsorption process of bolaamphiphiles on solid surface; (2) aggregation behaviors in the bulk solution, including (i) the superior vesicle formation ability, (ii) superior vesicle stability, (iii) dynamic morphology of the aggregates, and (iv) tunable morphologies; (3) perspective for the future.

© 2009 Elsevier Inc. All rights reserved.

## 1. Introduction

Bolaamphiphiles, abbreviated as *bolas*, i.e., bipolar amphiphiles with two polar heads connected by one or two long hydrophobic spacers, have attracted increasing attention since the early 1980s [1–5], when scientists found them in the membrane of archaeobacteria. Owing to the presence of membrane spanning bolaamphiphiles, these bacteria can sustain harsh environments, such as high salt concentrations, extreme temperatures, or very acidic environments [6–8]. The superior stability of the membrane of the archaeobacteria was attributed to the membrane spanning bolas that act as rivets to keep the bilayer together [9,10] (cf. Fig. 1a). The advantages of the bipolar structure of the bolas have stimulated an outburst of interest in this new type of amphiphiles in the recent 30 years. Since bolaamphiphiles are difficult to isolate from natural membranes, scientists have resorted to chemical synthesis to mimic natural bolaamphiphiles [1–8]. A large variety of bolaamphiphiles of different structures have been produced so far. Fig. 1b illustrates the structure of some typical bolas. For detailed structures of various bolas, one can refer to literatures 3 and 5.

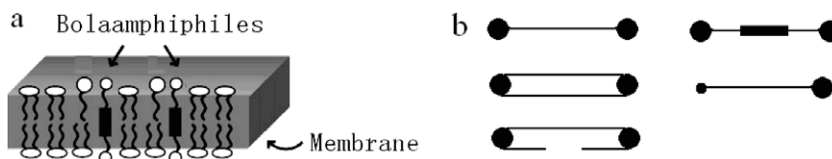
However, no much progress was achieved in regard to fabrication of artificial membranes with superior stability under harsh conditions so far. In contrast, investigation on the aggregation, i.e., self-assembled behaviors of bolaamphiphiles has become prosperous [1–5]. Starting from the simplest bolaamphiphiles, e.g., those with two polar heads connected by one hydrocarbon chain

[11–14], scientists have established the basic physical chemistry of these compounds in aqueous solution. It was found that bolaamphiphiles have much weaker surface activity but stronger aggregation ability which is characterized by much higher surface tension but lower CMC (critical micelle concentration) than their conventional counterparts with the same hydrocarbon/head group ratio [11–14]. Moreover, with the development in synthesis of more complicated bolas [3,5], abundant self-assembled structures from this class of amphiphiles have been observed. This is mainly attributed to their structural analogy to A-B-A type triblock copolymers, which allows for versatile modification of the molecules. By variation of both the structure of the head groups and that of the spacers, one can have a judicious choice on fabrication of bolaamphiphiles with special aggregation properties. This usually cannot be achieved in simple conventional surfactant systems. So far, various self-assembled structures, including nanofibers [15–18], nanotubes [19–21], ribbons [22], cylinders [23], disks [24], vesicles [25–27], as well as hydrogels [28–30] and liquid crystals [31–33], have been fabricated in bola systems. In addition, bolaamphiphiles were also used in template synthesis [34–36]. Clearly, the self-assembled properties of bolaamphiphiles have become very important both in terms of formation of soft condensed matter and fabrication of advanced hard materials.

Regarding amphiphiles with aggregation behaviors, the mixed systems of cationic/anionic (catanionic) surfactant solutions, have more advantages than the single ones. For instance, spherical and worm-like micelles, or vesicles can be obtained simply by tuning the mixing ratio [37–40] and other environmental conditions [41–45]. Especially, the report of spontaneous formation of vesicles

\* Corresponding author. Fax: +86 10 6275 1708.

E-mail addresses: jbhuang@pku.edu.cn, JBHuang@chem.pku.edu.cn (J. Huang).



**Fig. 1.** (a) Conformation of bolas in the membrane of *Archaea*; (b) illustration of structure of bolaamphiphiles. The skeleton structures represent symmetrical bolas with flexible single, double, half-loop (left column top down), rigid (right upper), spacer chain, and asymmetrical head groups (right down).

in the cationic surfactant solutions of single tailed CTAT/SDBS system [46] overturned the well-accepted opinion that only lipid molecules with double tails can form vesicles upon sonication. From then on, profound researches on the cationic surfactant systems have been carried out by many groups in the world [47–63].

Under this background, researches on the mixed systems of bolas and oppositely charged conventional surfactant systems have attracted increasing attentions [64–73]. Many interesting novel results have been reported. However, when compared with many reviews on either the single bolaamphiphilic systems or cationic surfactant mixed ones, no specific reviews on the mixed systems of bolaamphiphile/oppositely charged surfactant have been made. Therefore, in this article, we aim to summarize the recent advances in the research on the bolaamphiphile/oppositely charged conventional surfactant mixed systems. The following facets are included: (1) surface properties, (2) aggregates in the bulk solution, and (3) perspectives for the future. We hope to convey an overall view for the progress in this field, though we may not cover all the details of the literature results. Nevertheless, this is a specific review on the mixed systems of bolaamphiphile/oppositely charged surfactant. The corresponding structures and abbreviations of the bolaamphiphiles as well as that of the conventional surfactants mentioned in this paper are given in Figs. 2 and 3.

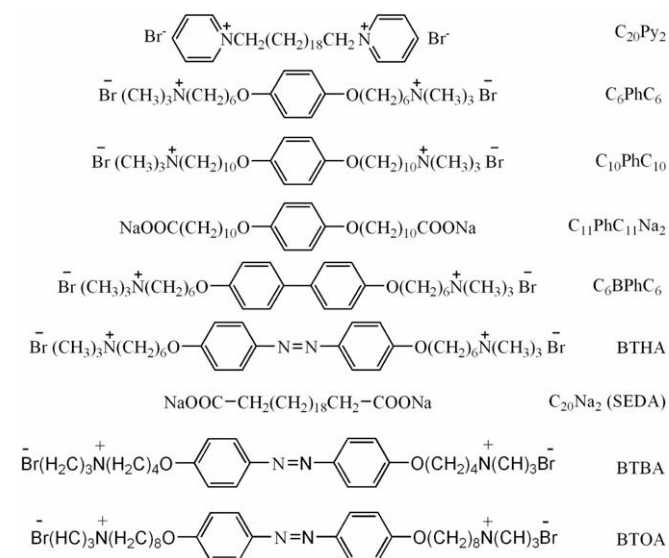
## 2. Surface properties

### 2.1. General properties

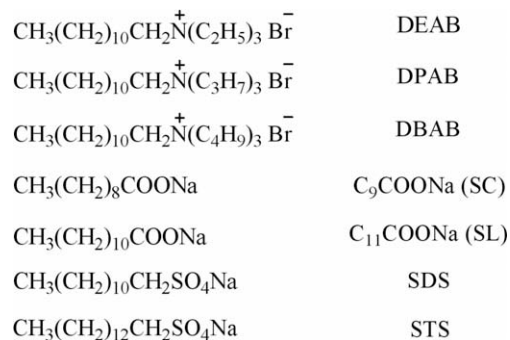
Usually, the single solution of a bolaamphiphile has very poor surface activity, i.e., its ability to decrease the surface tension of

water is weaker than that of conventional surfactants. This is due to the reverse U-shaped conformation of the bolas at the air/water interface (cf. Fig. 4a) when both the polar ends have to attach to water and the hydrocarbon spacers protrude into the air [11–14,74–77]. As a result, the outmost groups at the air/water interface are CH<sub>2</sub> from the spacer of the bolas instead of CH<sub>3</sub> from the conventional surfactants. Since the ability for CH<sub>2</sub> groups to decrease the surface energy is lower than that of CH<sub>3</sub> [78,79], the surface tension of water in bola systems cannot be lowered as much as that in conventional surfactant solutions. Actually, CH<sub>3</sub> groups have the lowest surface energy when compared with other hydrocarbon structures. Furthermore, the reverse U-shaped conformation results in a smaller surface excess [80], which disfavors lower surface tension as well. Upon mixing with oppositely charged surfactants, synergism effect occurs owing to the strong electrostatic attraction between the oppositely charged head groups. As a result, the average saturated surface excess is increased, and some CH<sub>3</sub> groups from the conventional surfactant participate in the outmost layer at the air/water interface (cf. Fig. 4b). Therefore, the surface tension was effectively lowered in the mixed systems. For example, the surface tension of the C<sub>20</sub>Py<sub>2</sub>/SDS and C<sub>6</sub>PhC<sub>6</sub>/SDS mixed systems at stoichiometric mixing ratio have been decreased 14 and 18 mN/m, respectively, when compared with that of the corresponding single bolas [68,80,81].

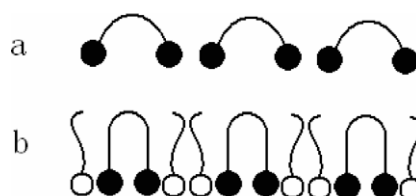
It should be pointed out that the reverse U-shaped conformation of bolaamphiphiles is usually formed at the air/water interface. In highly pressed LB films or Langmuir films, an upright



**Fig. 2.** Chemical structures and the corresponding abbreviations of synthetic symmetrical bolaamphiphiles.



**Fig. 3.** Chemical structures and corresponding abbreviations of conventional surfactants.



**Fig. 4.** Conformation of bolas at air/water interface under different conditions: (a) single solution; (b) mixed with oppositely charged surfactant.

conformation may be formed [82–84]. For instance, a chiral bolaamphiphilic *N,N'*-eicosanedioyl-di-L-glutamic acid (EDGA) anchored at the air/water interface at low pressures, while it stands up with only one head touching water and the other extruding into the air when the pressure exceeds the plateau [83] (Fig. 5).

## 2.2. Effect of rigid group on the surface property

The surface properties of bolaamphiphiles' solution depend strongly on their spacer structure. For most bolas with flexible spacer, one can find only one break, which is CMC, in the surface tension curve [68]. However, when considerable rigidity, usually at least a biphenyl group, is introduced to the spacer, one may get two breaks in the surface tension curves [69,71,85] (cf. Fig. 6). This has been proved due to the formation of aggregates before a real CMC is arrived [69,71]. Introduction of bulky rigid groups into the spacer chain seems to enhance the aggregation ability of bolas. It has been reported that cylinder, disk- or rod-like structures can be obtained in the single solution of bolaamphiphile that contains rigid groups in the spacer chain [17,23,34,84]. This was attributed to the  $\pi$ - $\pi$  stacking between these rigid groups. If such aggregation was prohibited by addition of alcohol or formamide, only one break was observed in the surface tension curve [71] (cf. Fig. 7).

In addition, the surface tension above CMC decreases upon addition of short-chained alcohol to the mixed system [85] (cf. Fig. 8), whereas that for the mixed systems of conventional cationic surfactants was found to increase under the same treatment. This significantly different alcohol effect on the surface tension was again attributed to the molecular conformation at the air/water interface. For the conventional cationic surfactant systems, the hydrocarbon chains are densely packed at the air/water interface. Addition of alcohol disfavors the densely packing of the chains due to the voids produced by the adsorbed short alcohol molecules in the adsorption layer, and the surface tension increases. In contrast, the packing of molecules in the surface layer of the bola/conventional surfactant mixed solutions is much looser due to the bulky reverse U-shaped conformation of bolaamphiphiles. When alcohol molecules enter the adsorption layer, it may take the free space in the loose surface layer. As a result, there are more  $\text{CH}_3$  groups in the adsorption layer, and the surface tension is decreased.

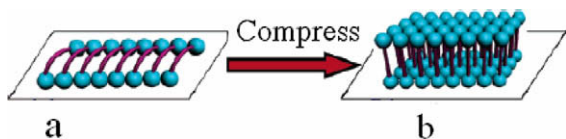


Fig. 5. Conformation change of bolaamphiphile *N,N'*-eicosanedioyl-di-L-glutamic acid (EDGA) at different pressures. Adapted from Ref. [83].

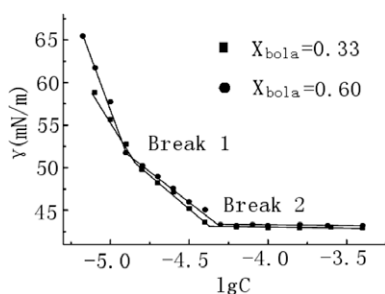


Fig. 6. Two breaks in the surface tension curve of rigid group containing bola  $\text{C}_6\text{BPhC}_6$  in the mixed systems with SDS. The occurrence of two break points is regardless of mixing ratio. Adapted from Ref. [69].

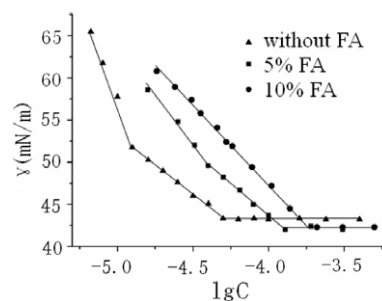


Fig. 7. Surface tension curves  $\text{C}_6\text{BPhC}_6/\text{SDS}$  mixed systems with and without formamide (FA) at  $30.0\text{ }^\circ\text{C}$ ,  $X_{\text{bola}} = 0.60$ . Adapted from Ref. [71].

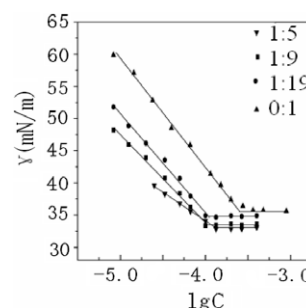
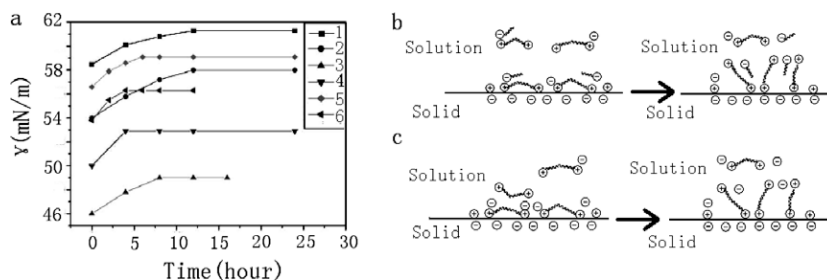


Fig. 8. Surface tension of 1:2  $\text{C}_{20}\text{Na}_2/\text{DEAB}$  system (pH 9.2) in ethanol/water with various volume ratios. Adapted from Ref. [85].

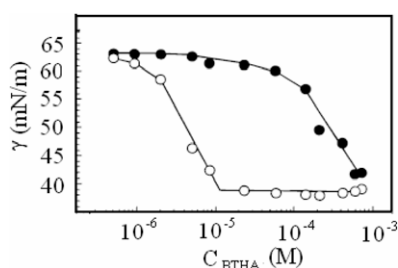
## 2.3. Dynamic surface tension

Adsorption of surfactant molecules on surfaces takes time. The time for a conventional surfactant to reach equilibrium is usually less than 30 min. In this process one may observe a decrease of the surface tension owing to a bigger surface excess at equilibrium state. However, in the mixed solution of cationic bola/anionic conventional surfactant, a slow time effect as long as several hours was observed (cf. Fig. 9); when equilibrium was reached, one found an increase of the surface tension [86]. This was only observed in single cationic or cationic bolaamphiphile/anionic conventional surfactant mixed systems, but not found in those in single anionic or anionic bola/cationic conventional surfactant solutions [86]. The reverse time effect is attributed to a slow competition process: both the anionic counter ions or conventional surfactant and the negatively charged vessel wall tend to bind with cationic bolaamphiphiles. It was the competition that makes this process extremely slow. In dilute solutions, the significant adsorption of bolas on the glass vessel decreases the bulk concentration, which lowers the surface excess. Therefore, the surface tension increases. Obviously, the slow increase of the surface tension can be overcome either by increasing the bulk concentration or prerinsing the glassware before use, so that the adsorption on the glass wall is negligible [86].

Dynamic surface tension can also be resulted from the change in the mixed aggregates in the bulk solution of a cationic bola/surfactant system. For instance, Abbott et al. reported that the surface tension of the UV-illuminated BTHA/SDS solution can be up to 25 mN/m lower than that of without any illumination [87] (Fig. 10). Since BTHA molecules contains azobenzene group, it underwent *trans*-*cis* isomerization upon UV illumination. Light scattering experiments revealed that aggregates before and after UV illumination are of similar sizes, but the number density of the aggregates was almost halved. This demonstrates that after illumination, more surfactant molecules were released from the aggregates, so that they migrated to the surface and lowered the



**Fig. 9.** (a) Variation of surface tension in the stoichiometric bola/oppositely charged surfactant mixed systems ( $X_{\text{bola}} = 0.33$ ) with time. Symbols represents: 1,  $C_{20}Py_2$ ,  $2.5 \times 10^{-5}$  M; 2,  $C_{20}Py_2/SDS$ ,  $6.25 \times 10^{-6}$  M; 3,  $C_{20}Py_2/SDS$ ,  $2.25 \times 10^{-5}$  M; 4,  $C_{20}Py_2/C_{11}COONa$ ,  $4 \times 10^{-5}$  M; 5,  $C_6PhC_6/SDS$ ,  $7.84 \times 10^{-5}$  M; 6,  $C_6BPhC_6/SDS$ ,  $9.53 \times 10^{-6}$  M; (b and c) possible mechanism for adsorption of bolaform cationic amphiphiles in mixed systems (b) and of single flexible bolaform cationic amphiphiles systems (c) on the surface of glass. Adapted from Ref. [86].



**Fig. 10.** Surface tensions of aqueous solutions of mixtures of BTHA and SDD (1.6 Mm) measured as a function of BTHA concentration before (filled circles) and after (open circles) illumination with UV light. Experiments were carried out with du Nouy ring method. Adapted from Ref. [87].

surface tension. In addition, the lowest surface tension occurred at BTHA/SDS molar ratio of 1:2, which is the charge-neutral mixing between the cationic and anionic heads of BTHA and SDS. In contrast, no significant surface tension change was observed in the BTHA single solution upon UV illumination, as is a strong support for the conclusion that the surface tension change in the BTHA/SDS mixed solution was induced by the change of aggregates.

### 3. Self-assembled structures in solution

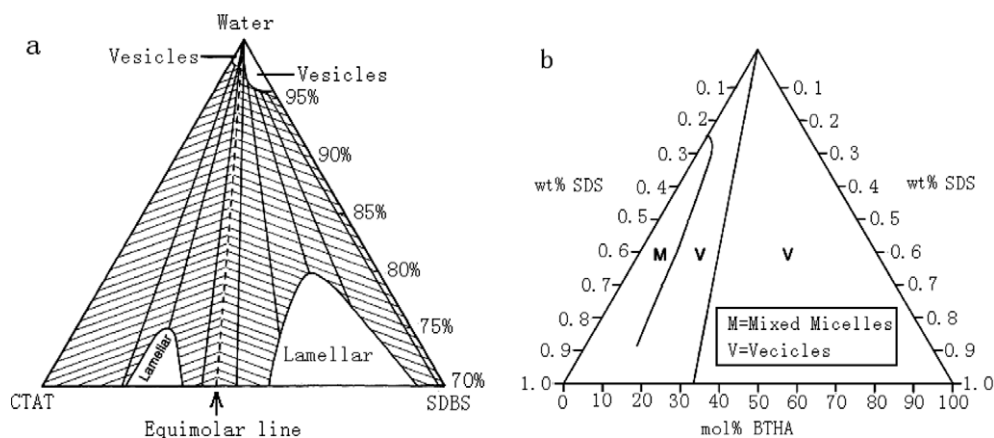
#### 3.1. Superior ability in vesicle formation

The reminiscent feature of the mixed systems of a bolaamphiphile and an oppositely charged conventional surfactant is their superior ability in vesicle formation. Since the first report of vesi-

cles in the oppositely charged surfactant mixed systems by Kaler et al. [46], formation of vesicles was observed in a lot of surfactant mixed systems. However, the common problem is that the suitable mixing ratio range for vesicles formation is very narrow. Actually, micelles and precipitates govern most of the territory in the phase diagram, and the vesicle region is only a small corner in the diagram (cf. Fig. 11a) [46]. This shortcoming can be easily overcome in the bolaamphiphile/oppositely charged surfactant systems. One can get a broad mixing ratio range of vesicle formation, including the exact equimolar ratio and those with large excess of one component. For example, we have observed the presence of vesicles in the broad range of  $X_{\text{bola}} = 0.05\text{--}0.90$  in the mixed system of  $C_{10}PhC_{10}/C_9COONa$  [72] (Table 1 and Fig. 12). Precipitates at equimolar ratio are effectively avoided by the presence of counterions and the extra addition of NaBr to the system.

A broad mixing ratio range for vesicle formation was also observed by Abbott et al. [66,67]. In their SDS/BTHA mixed systems, vesicles were found in about 90% of the composition diagram in the fresh solutions (cf. Fig. 11b). Six months later, some precipitates were observed coexisting with vesicles in some area. This could probably be avoided by addition of inorganic salt. Nevertheless, it is obvious that the mixed systems have very good vesicle formation ability.

The vesicles formed in the above systems are of several tens nanometers in diameter. Our XRD results revealed that the membrane thickness is almost equal to the length of the bola molecules  $C_nPhC_n$  [72]. This indicates that these bola molecules containing rigid groups span the vesicle membrane so as to rivet the surfactant bilayer together (cf. Fig. 13a) [72]. Recently, the spanning conformation of bolas in the vesicle membrane was confirmed by small

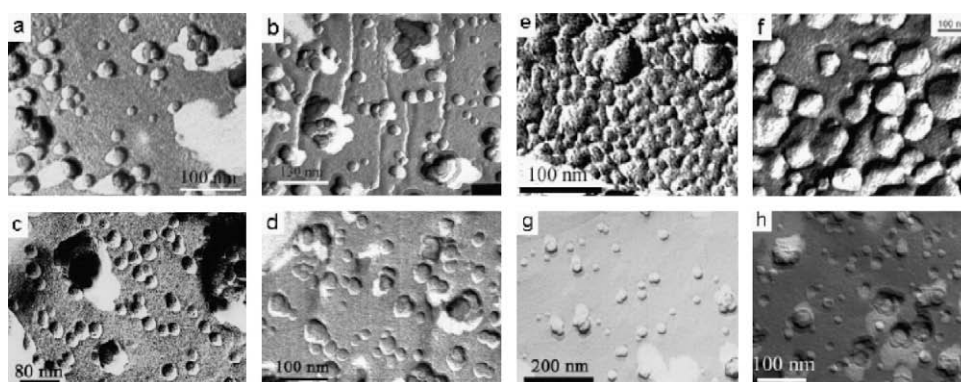


**Fig. 11.** Phase diagram for: (a) conventional cationic surfactant mixed system CTAT/SDS, in which vesicles were formed in dilute solutions at mixing ratios deviate from the equimolar line. The dash area indicates precipitation region. Adapted from Ref. [46]. (b) Bolaamphiphile BTHA and oppositely charged SDS mixed system, in which the vesicles were presence at  $X_{\text{BTHA}} = 0.15\text{--}1$ . Adapted from Ref. [66].

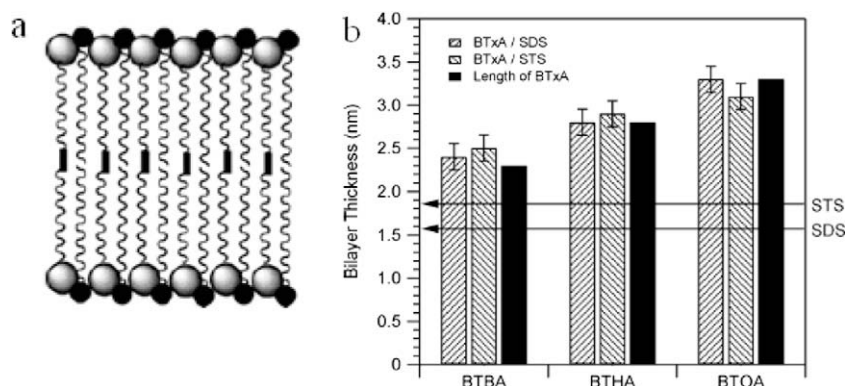
**Table 1**  
Vesicles formed in cationic bola/conventional surfactant systems. Adapted from Ref. [72].

System	$C_T$ (M)	$X_{\text{bola}}$	TEM observation	Vesicle diameter (nm)
Ia/SDS	$1.0 \times 10^{-3}$	0.05–0.82	+	10–30
Ia/C <sub>9</sub> COONa	$1.0 \times 10^{-2}$	0.05–0.82	+	20–40
Ia/C <sub>11</sub> COONa	$1.0 \times 10^{-2}$	0.05–0.82	+	20–40
Ib/SDS	$1.0 \times 10^{-4}$	0.05–0.91	+	10–50
Ib/C <sub>9</sub> COONa	$1.0 \times 10^{-3}$	0.05–0.90	+	20–50
Ib/C <sub>11</sub> COONa	$1.0 \times 10^{-3}$	0.05–0.90	+	20–50
Ic/SDS	$1.0 \times 10^{-3}$	0.33–0.82	+	20–100
Ic/C <sub>9</sub> COONa	$1.0 \times 10^{-2}$	0.33–0.82	+	10–80
Ic/C <sub>11</sub> COONa	$1.0 \times 10^{-2}$	0.33–0.82	+	10–80

Ia, C<sub>6</sub>PhC<sub>6</sub>; Ib, C<sub>10</sub>PhC<sub>10</sub>; Ic, C<sub>6</sub>BPhC<sub>6</sub>; +, vesicles observed.



**Fig. 12.** Freeze-fracture replica of the vesicles formed in cationic bola/oppositely charged conventional surfactant mixed systems. (a) Ia/SDS,  $X_{\text{bola}} = 0.33$ ; (b) Ia/SDS,  $X_{\text{bola}} = 0.82$ ; (c) Ia/C<sub>9</sub>COONa,  $X_{\text{bola}} = 0.83$ ; (d) Ib/SDS,  $X_{\text{bola}} = 0.91$ ; (e) Ib/SDS,  $X_{\text{bola}} = 0.60$ ; (f) Ic/SDS,  $X_{\text{bola}} = 0.60$ ; (g) Ic/C<sub>9</sub>COONa,  $X_{\text{bola}} = 0.83$ ; (h) Ic/C<sub>11</sub>COONa,  $X_{\text{bola}} = 0.83$ . Adapted from Ref. [72].



**Fig. 13.** (a) Proposed molecular conformation in the vesicle membrane of bola/oppositely charged surfactant mixed systems. Adapted from Ref. [72]. (b) Comparison of the measured vesicle bilayer thickness to the molecular length of surfactant for vesicles formed from mixtures of BTxA and SDS or STS. Adapted from Ref. [89].

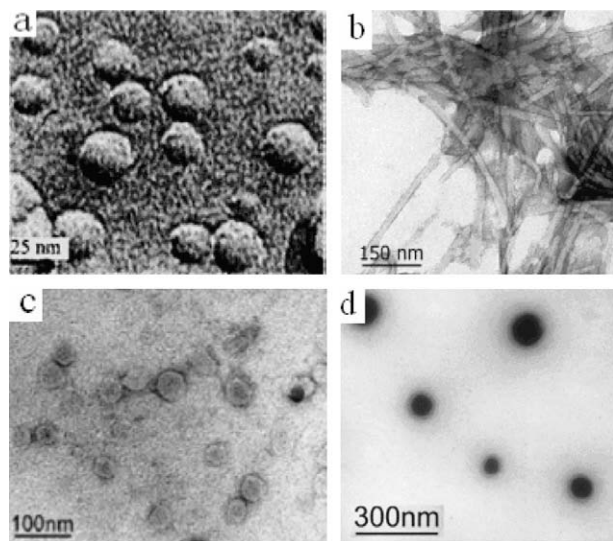
angle neutron (SANS) measurements as well [88,89]. Abbott et al. inferred from the form factor fits that the bolaform molecules BTxA ( $x = B, H, O$ ) span the bilayer of SDS or STS, and constrain the bilayer thicknesses to the end-to-end lengths of the bolaform surfactants (cf. Fig. 13b) [89].

The superior ability in vesicle formation was also found for insoluble bolas with a long alkyl spacer chain. For example, the carbonate bola C<sub>20</sub>Na<sub>2</sub> itself is almost insoluble in water, but its solubility can be increased about 20 times in the cationic DEAB solution. Meanwhile, spherical vesicles with a diameter of about 60 nm were formed (cf. Fig. 14a).

Besides vesicles, other types of structure can be formed as well by addition of the water-insoluble bola into an oppositely charged conventional surfactant solutions. Typical examples are those

aggregates observed in the mixed systems of the anionic bolaamphiphile C<sub>11</sub>PhC<sub>11</sub>Na<sub>2</sub> and the conventional cationic DE/P/BAB. The C<sub>11</sub>PhC<sub>11</sub>Na<sub>2</sub> powder, which is hardly soluble in pure water, disappeared quickly in the DEAB solution. Meanwhile, ribbon-like structures were observed after C<sub>11</sub>PhC<sub>11</sub>Na<sub>2</sub> is completely dissolved (cf. Fig. 14b). Upon increasing the size of the headgroup of DEAB to DPAB and DBAB, vesicles were obtained (cf. Fig. 14c and d). This result demonstrates that the ‘insoluble’ bolas induce the formation of proper self-assembled structures, which in turn promote the solubility of the bolas.

If counter ions are removed from the system, one obtains ion pairs of bola–surfactants. In this case, the mixing ratio between the bola ions and the surfactant ions is fixed at stoichiometric ratio, and the formation of vesicles is supposed to be facilitated since ion



**Fig. 14.** Increase of solubility of insoluble bolas by formation of aggregates with oppositely charged conventional surfactants. (a)  $C_{20}Na_2/DEAB$ , 1:2. Adapted from Ref. [68]; (b)  $C_{11}PhC_{11}Na_2/DEAB$ , 1:4. (c)  $C_{11}PhC_{11}Na_2/DPAB$ , 1:4; (d)  $C_{11}PhC_{11}Na_2/DEAB$ , 1:4. (b–d) Adapted from Ref. [72].

pairing brings about ca.  $5 \text{ kcal mol}^{-1}$  stabilization energy [90]. Bhattacharya et al. found that the vesicles in the dialkylcarbonate benzene/CTA ion pair bola/surfactant systems are multilamellae (cf. Fig. 15) [90]. Depending on the relative position of the two alkyl carbonate chains on the benzene ring, vesicles with diameters of about 51, 98, 125 nm were formed. Upon comparison of the molecular length and the membrane thickness, tilted bilayer arrangement was suggested.

Salt free ion pairs bola/conventional surfactants can also be synthesized by simply mixing dicarboxylates and amine surfactants [91]. Proton transfer between the carboxylic acid and the amine produces a catanionic pair. Vesicles can be formed when the alkyl chain between the two carboxylate groups reaches 6  $CH_2$ . Molecular models demonstrate that for shorter alkyl chain of 3 and 5, the catanionic pairs take a ball-like conformation which disfavors for vesicle formation (Fig. 16).

### 3.2. Vesicles with superior thermo-stability

The initial pulse on the research of bolaamphiphiles is to fabricate artificial vesicle membranes that can sustain harsh environments, such as high temperature. But efforts in this respect do not end with considerable success in single bola systems. However, in the catanionic systems of a bolaamphiphile and a conventional surfactant, superior thermo-stability of vesicles in aqueous solution was easily obtained. We found that the vesicles formed by  $C_{20}Na_2/DEAB$  are still stable at temperature around  $90^\circ\text{C}$  (cf. Fig. 17a and b) [70]. No endothermic peak was observed and no

conformation change of the alkyl chains occurred in the temperature range of  $10\text{--}90^\circ\text{C}$  (cf. Fig. 17c). The predominant all *trans* conformation of the  $CH_2$  groups in the membrane kept perfectly, which is characterized by the stable position of the asymmetric and symmetric vibration peak at  $2918$  and  $2847 \text{ cm}^{-1}$ , respectively (cf. Fig. 17d). This indicates that the lyophilic (hydrophobic) interaction between the long alkyl chains plays a very crucial role in resisting high temperature.

Thermo-stable vesicles were also obtained in the system of other bolaamphiphile/SDS mixed systems [72]. But we found that in case of using cationic bolaamphiphiles containing benzyl ring in the spacer, the mixed systems with carbonate alkyl anionic surfactant do not produce such thermo-stability. This is probably due to the following two reasons: one is the much weaker interaction of the quaternary ammonium group with the carbonate group than that with sulfate group [72]; the second is the presence of benzene ring in the spacer chain that might be not suitable for a densely packing of the hydrocarbon chains in the membrane. It seems that both the electrostatic and the hydrophobic interaction in the oppositely charged bola/surfactant mixed systems play key roles in fabrication of thermo-stable membrane. Therefore, we expect that by careful design and choice of oppositely charged bola/surfactant mixed systems, artificial membranes that can sustain harsh environments can be produced.

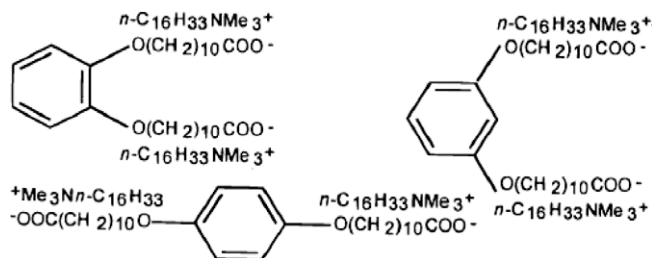
### 3.3. Morphology of dynamic aggregates

The morphology of the self-assembled structures in some oppositely charged bola/conventional surfactant mixed systems is time-dependent. For example, spherical vesicles were found in the mixed system of  $C_{20}Na_2/DEAB$  aged less than 6 months (cf. Fig. 14a); whereas tube-like structures were observed one year later (cf. Fig. 18a). This is probably due to the slow dynamics of bolaamphiphiles in the membrane. It could be that at the beginning some U-shaped bolas together with predominant stretched ones coexist in the membrane (cf. Fig. 18b). Then the U-shaped ones gradually change their conformation with time. Because considerable energetic barrier should be surpassed when the hydrophilic head groups of bola traverse the hydrophobic membrane, this conformation change process is very slow.

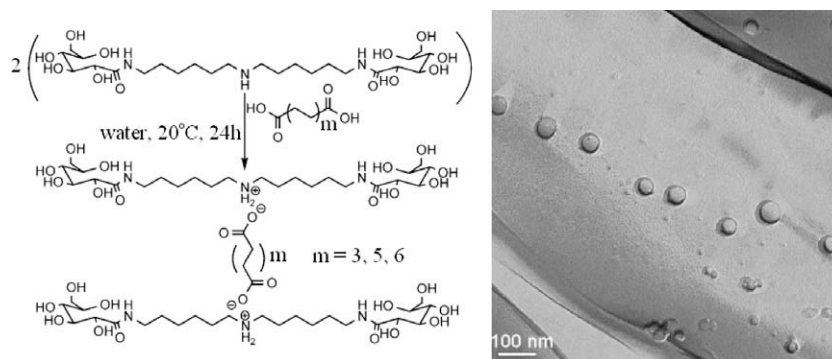
We also observed time-dependent morphologies in the  $C_6BPhC_6/SDS$  mixed system (cf. Fig. 19) [73]. Vesicles are the initially formed aggregates (cf. Fig. 19a), whereas 3–5 days later, the vesicle membrane starts fusion (cf. Fig. 19b). Within 10 days, most of the spherical vesicles have transformed into tube-like structures (cf. Fig. 19c and d). Heating can accelerate this vesicle-tube transformation process. In addition, Hubbard et al. observed precipitates in the 6 months aged vesicle solutions [66]. This also revealed the dynamic feature of the self-assembled structures in the oppositely charged bola/conventional surfactant mixed systems. Such a feature is probably related to the bipolar structure of bolas and the change of their conformation in the mixed monolayer membrane.

### 3.4. Tunable morphologies of the self-assembled structures

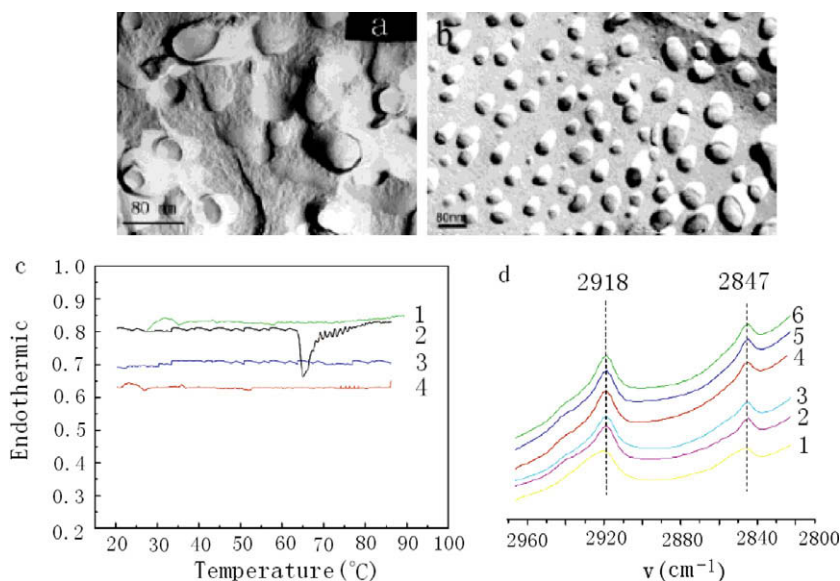
Although vesicles are the very common structures introduced so far, transition from vesicles to other structures can be realized by tuning the environmental or the structural factors of the constituent surfactants. Many strategies in conventional surfactant systems are applicable for the oppositely charged bola/conventional surfactant mixed systems. For instance, once azobenzene group is introduced to a bola molecule, one can get light tunable self-assemblies in the bola/conventional surfactant mixed system. An excellent example is given by Abbott et al. [66,67]. They first obtained vesicles by mixing SDS with *trans* BTHA, which is a bola type molecule containing azobenzene group. Upon UV irradiation



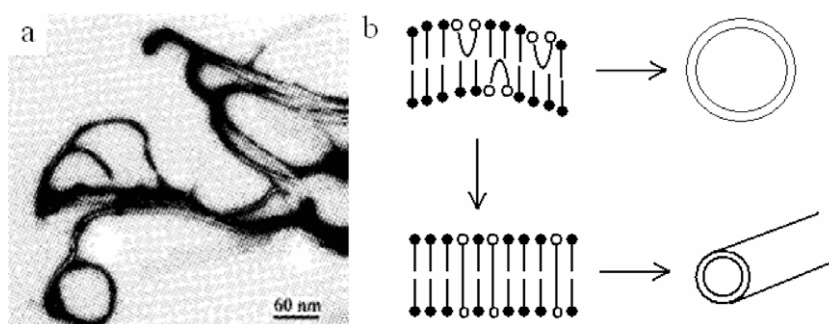
**Fig. 15.** Ionpairs of bola/surfactants. Adapted from Ref. [90].



**Fig. 16.** Preparation of salt free catanionic pair of bola/surfactant and the vesicles formed by the catanionic pair of  $m = 6$ . No vesicles were formed at  $m = 3$  and 5. Adapted from Ref. [91].



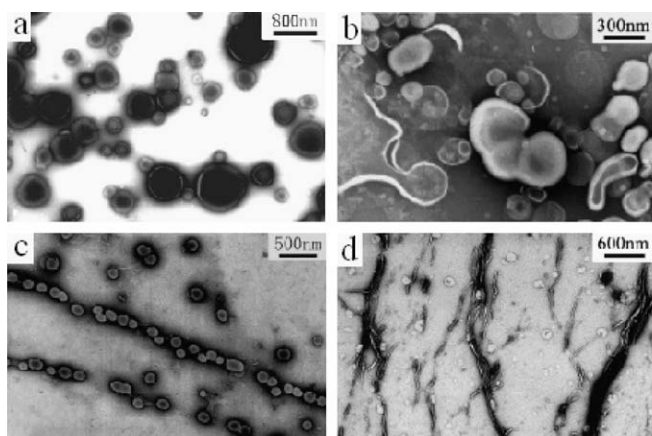
**Fig. 17.** Freeze-fracture replica of vesicles in  $C_{20}Na_2/DEAB$  system at 50 (a) and 80 °C (b), respectively; (c): ART-FT-IR spectra of  $CH_2 \nu_{as}$  and  $\nu_s$  for the vesicle suspensions at different temperatures: curves 1–6 corresponds to 20, 30, 40, 50, 80, and 90 °C; (d) DSC curves of the vesicle suspensions ( $C = 0.02$  M), curves 1–3 corresponds to systems of with mixing ratios of  $X_{bola} = 0.33, 0.25, 0.125$ . Curve (d) is a contrast DSC curve for  $C_{11}COONa/DEAB$  vesicles system ( $C = 0.02$  M). Adapted from Ref. [70].



**Fig. 18.** (a) Tube-like structures formed in the one year aged  $C_{20}Na_2/DEAB$  mixed system. (b) Illustration of the possible mechanism of vesicle–tube transition. Adapted from Ref. [68].

of the vesicle solution to allow the formation of *cis* azobenzene isomers of BTHA, a transition from vesicles to rod-like micelles was observed (cf. Fig. 20). This morphology transition can be explained by using critical molecular packing parameter  $P$ , which is defined as  $P = v/a_0l$  [92,93]. Here,  $v$  is the volume of the hydrophobic section of an amphiphilic molecule,  $a_0$  the effective area of head groups in the aggregates, and  $l$  the length of the hydrophobic chain.

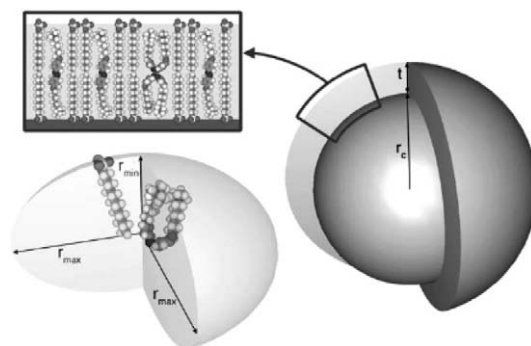
Since the *cis* isomers of BTHA take a U-shaped conformation in the molecular aggregates, both of the two heads of BTHA locate in one side of the membrane. This means that the area of the head groups is doubled while keeping the same volume and length of the hydrophobic chain. As a result, the critical molecular packing parameter has been halved according to the relation of  $P = v/a_0l$ . This results in the formation of self-assembled structures with high



**Fig. 19.** TEM micrographs for the mixed system of  $C_6BPhC_6/SDS$  ( $X_{bola} = 0.60$ ,  $C = 1 \times 10^{-4}$  M) at 22 °C: (a) within 3 days; (b) 3–7 days; (c and d) within the third week. Adapted from Ref. [73].

curvatures, which are the rod-like micelles in their case. It is interesting to find that upon irradiation the rod-like micelles with visible light, vesicles reoccurred owing to the transformation of *cis* into *trans* isomers of the BTHA. But this reversible vesicle to rod-like micelle transition induced by UV/visible light can be achieved only for systems rich in SDS. For systems rich in BTHA, precipitates occurred irreversibly. Surprisingly, in the same system, but at a different molar ratio of SDS/BTHA = 4.8, Baglioni et al. reported the transition between vesicles and oblate micelles (cf. Fig. 21) [88]. This is probably that the aspect ratio of the micelles is very sensitive to the mixing ratio.

Adjustment of the packing parameter by modifying environmental conditions can also be used to tune the morphology of the aggregates in the oppositely charged bola/surfactant mixed systems [21]. For instance, addition of alkyl chain alcohols to the micelle forming bola/surfactant mixed systems can lead to transition from micelles to vesicles and tubes; shielding the excess charge in the mixed micelles or vesicles by additional inorganic salt drives a transformation of the structures with smaller  $P$  to those with larger  $P$ ; increasing the headgroup size of the oppositely charged conventional surfactants results in self-assemblies with larger curvature (cf. Fig. 14b–d) [70]. Obviously, most the structural and the environmental factors that affect the molecular packing parameter can be used in the oppositely charged bola/conventional surfactant systems. One exception is the pH factor,



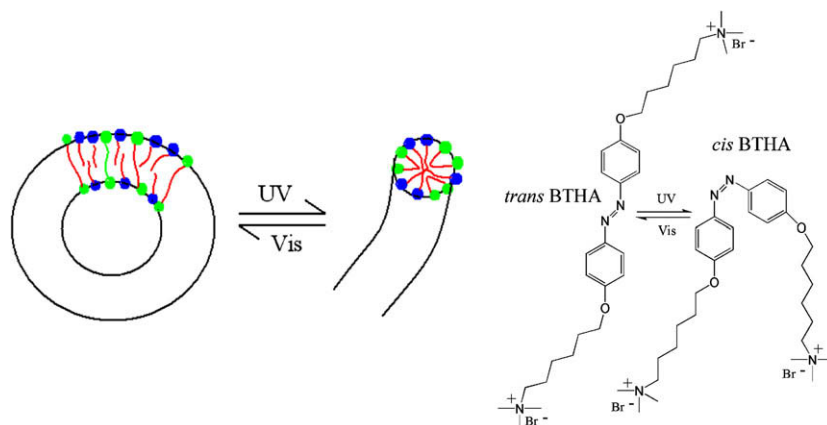
**Fig. 21.** Illustration of the conformation change induced transition between vesicles and oblate micelles upon alternatively irradiation with UV and visible light on BTHA/SDS vesicles at mixing ratio of 1/4.8. Adapted from Ref. [88].

which loses its ability in tuning the morphology of the self-assembled structures in these systems, since the electrostatic interaction is much stronger than any interaction change brought up by pH. This is, on the other side, good for fabrication of vesicles that can endure very acidic or alkaline conditions. Recently,  $\beta$ -CD is reported to form complexes with some bolaamphiphiles [94,95]; it is therefore might be potentially used to tailor the morphology of the aggregates in the cationic bola/surfactant mixed systems, as they have successfully done in conventional cationic surfactant mixed systems [96].

In addition, the morphology of the self-assembled structures in some bola systems depends also on concentrations. As mentioned in Section 2.1, two breaks occur in the surface tension curves of the  $C_6BPhC_6/SDS$  mixed systems. The first break at much lower concentrations is caused by the formation of tube-like structures (cf. Fig. 22a and b), while the second break at higher concentrations is resulted from vesicles (cf. Fig. 12f) [69,71]. The concentration-dependent aggregation behavior was also found in the  $C_{20}Na_2/DEAB$  mixed systems [68,72]. At very low concentrations, one observed vesicles (cf. Figs. 14 and 17a), whereas at much higher concentrations, network structures were observed (cf. Fig. 22c) [68].

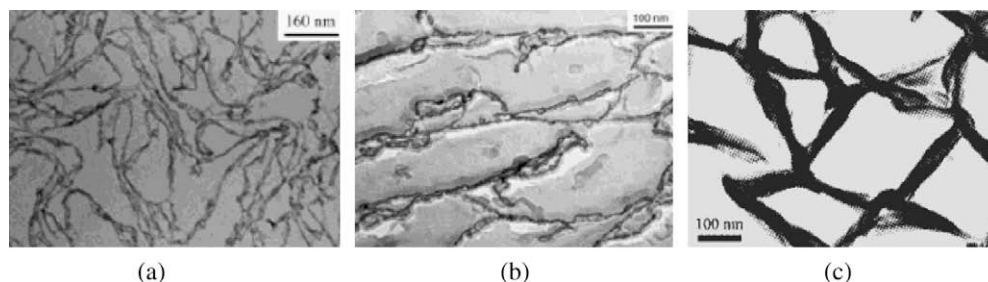
#### 4. Perspective and conclusions

The oppositely charged bola/surfactant mixed systems are very promising in fabrication of molecular devices and advanced functional materials. The examples given in this review covers only a small fraction of bolaamphiphiles that have been synthesized.



**Fig. 20.** Illustration of the transformation between vesicles and rods upon alternatively irradiation with UV and visible light on BTHA/SDS vesicles at mixing ratio of 15/85. Adapted from Ref. [67].





**Fig. 22.** Freeze replica TEM micrographs for aqueous  $C_6BPhC_6/SDS$  mixed solutions. (a)  $C_6BPhC_6$ :  $SDS = 1:2$ ,  $C_{total} = 5.0 \times 10^{-5}$  M. Adapted from Ref. [69]. (b)  $C_6BPhC_6$ :  $SDS = 3:2$ ,  $C_{total} = 6.0 \times 10^{-5}$  M. Adapted from Ref. [69]. (c)  $C_{20}Na_2$ :  $DEAB = 1:2$ ,  $C_{total} = 0.01$  M. Adapted from Ref. [68].

Much more systems with oppositely charged conventional surfactant have not been explored yet. We expect that more bolaamphiphiles with special functional groups will bring up unexpected surprises to the bola/oppositely charged conventional surfactant mixed systems. For instance, modifying the head group structure of bolas may produce significant difference in the morphology of the aggregates in the bola/oppositely charged surfactant mixed systems, as has been observed by us in the gemini/oppositely charged surfactant mixed systems [97]. Using bolas containing special functional groups may endow the oppositely charged bola/surfactant mixed systems interesting optical, electronic or magnetic responsive properties. If redox active group, such as ferrocenyl head or disulfide bond, is introduced to a bola [98,75,99], the mixed systems may display redox switchable self-assembled structures. It will be also very interesting to exploit the host–guest chemistry to form catanionic system of bola/surfactant mixed systems. A good system may be bola molecules with crown ether heads, which can host ionic surfactants such as SDS [100]. The sodium ions released from the SDS will be entrapped into the cavity of the crown ether, which charge up the bola form surfactant so as to form ion pairs with the anionic SDS molecules. Such a catanionic bola/surfactant system is expected to be responsive with additional salt or special metal ions.

In addition, multilayers of oppositely charged bola/surfactants can be produced via layer-by-layer method. Usually, layer-by-layer method is applicable only for oppositely charged polyelectrolyte systems. By dipping a substrate alternatively into a positively and a negatively charged polyelectrolyte solution, respectively, multilayers can be produced. The bipolar nature of the bolaamphiphiles can also be used in this process. Multilayers containing bolaamphiphiles have been obtained by alternatively dipping a mica or silica wafer into the solution of a bola and an oppositely charged polyelectrolyte [101–104]. When photo-sensitive bola molecules are used, the optical properties of the film can be tuned reversibly [104]. It is can be expected that when the polyelectrolyte is substituted by conventional surfactants, layer-by-layer films might be produced as well. In this case, hydrophobic domain as well as functional groups can be introduced to the multilayers. This might open a new vista in the world of advanced functional materials. Anyway, compared with the tremendous amount of bolas that have been synthesized and the single systems of bolas that have been investigated, the oppositely charged mixed systems of bola/conventional surfactant are still a virgin to be explored. We expect to see more interesting work appears in this field in the near future.

## Acknowledgments

We thank the National Nature Science Foundation of China (NSFC) and the National Basic Research Program of China (2007CB936201) for the financial support.

## References

- [1] J.-H. Fuhrhop, J. Mathieu, *Angew. Chem. Int. Ed. Engl.* 23 (1984) 100.
- [2] G.H. Escamilla, G.R. Newkome, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1937.
- [3] J.-H. Fuhrhop, T.Y. Wang, *Chem. Rev.* 104 (2004) 2901.
- [4] T. Benvegnu, M. Brard, D. Plusquellec, *Curr. Opin. Colloid Interface Sci.* 8 (2004) 469.
- [5] A. Meister, A. Blume, *Curr. Opin. Colloid Interface Sci.* 12 (2007) 138.
- [6] G.D. Sprott, *J. Bioenerg. Biomembr.* 24 (1992) 555.
- [7] A. Gambacorta, A. Gliozzi, M. De Rosa, *World J. Microbiol. Biotechnol.* 11 (1995) 115.
- [8] K. Yamauchi, M. Kinoshita, *Prog. Polym. Sci.* 18 (1993) 763.
- [9] J.L. Gabriel, P.L.G. Chong, *Chem. Phys. Lipids* 105 (2000) 193.
- [10] D.P. Holland, A.V. Struts, M.F. Brown, D.H. Thompson, *J. Am. Chem. Soc.* 130 (2008) 4584.
- [11] K. Ikeda, M. Yasuda, M. Ishikawa, K. Esumi, K. Meguro, W. Binana-Limbele, R. Zana, *Colloid Polym. Sci.* 267 (1989) 825.
- [12] R. Zana, S. Yiv, K.M. Kale, *J. Colloid Interface Sci.* 77 (1980) 456.
- [13] K. Meguro, K. Ikeda, A. Otsuji, M. Taya, M. Yasuda, K. Esumi, *J. Colloid Interface Sci.* 118 (1987) 372.
- [14] F.M. Menger, S. Wrenn, *J. Phys. Chem.* 78 (1974) 1387.
- [15] D.A. Jaeger, G.W. Li, W. Subotkowski, K.T. Carron, *Langmuir* 13 (1997) 5563.
- [16] K. Köhler, G. Förster, A. Hauser, B. Dobner, U.F. Heiser, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, H. Stettin, A. Blume, *Angew. Chem. Int. Ed.* 43 (2004) 245.
- [17] B. Song, H. Wei, Z.Q. Wang, X. Zhang, M. Smet, W. Dehaen, *Adv. Mater.* 19 (2007) 416.
- [18] S. Drescher, A. Meister, G. Graf, G. Hause, A. Blume, B. Dobner, *Chem. Eur. J.* 14 (2008) 6796.
- [19] N. Kameta, M. Masuda, H. Minamikawa, N.V. Goutev, J.A. Rim, J.H. Jung, T. Shimizu, *Adv. Mater.* 17 (2005) 2732.
- [20] M. Ambrosi, E. Fratini, V. Alfreðsson, B.W. Ninham, R. Giorgi, P.Lo. Nostro, P. Baglioni, *J. Am. Chem. Soc.* 128 (2006) 7209.
- [21] Y. Yan, W. Xiong, X.S. Li, T. Lu, J.B. Huang, Z.C. Li, H.L. Fu, *J. Phys. Chem. B* 111 (2007) 2225.
- [22] E. Lee, Z.G. Huang, J.-H. Ryu, M. Lee, *Chem. Eur. J.* 14 (2008) 6957.
- [23] S.C. Yin, B. Song, G.Q. Liu, Z.Q. Wang, X. Zhang, *Langmuir* 23 (2007) 5936.
- [24] B. Song, Z.Q. Wang, S.L. Chen, X. Zhang, Y. Fu, M. Smet, W. Dehaen, *Angew. Chem. Int. Ed.* 44 (2005) 4731.
- [25] K.N. Liang, Y.Z. Hui, *J. Am. Chem. Soc.* 114 (1992) 6588.
- [26] J.-H. Fuhrhop, J. Mathieu, *J. Chem. Soc., Chem. Commun.* (1983) 144.
- [27] X.F. Wang, Y.Z. Shen, Y. Pan, Y.Q. Liang, *Langmuir* 17 (2001) 3162.
- [28] K. Köhler, G. Förster, A. Hauser, B. Dobner, U.F. Heiser, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, H. Stettin, A. Blume, *J. Am. Chem. Soc.* 126 (2004) 16804.
- [29] K. Köhler, A. Meister, G. Förster, B. Dobner, S. Drescher, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, G. Hause, A. Blume, *Soft Matter* 2 (2006) 77.
- [30] M. Ávalos, R. Babiano, P. Cintas, A. Gómez-Carretero, J.L. Jiménez, M. Lozano, A.L. Ortiz, J.C. Palacios, A. Pinazo, *Chem. Eur. J.* 14 (2008) 5656.
- [31] N. Mizoshita, T. Seki, *Soft Matter* 2 (2006) 157.
- [32] X.H. Cheng, X. Dong, R. Huang, X.B. Zeng, G. Ungar, M. Prehm, C. Tschierske, *Chem. Mater.* 20 (2008) 4729.
- [33] S. Das, N. Gopinathan, S. Abraham, N. Jayaraman, M.K. Singh, S. Krishna Prasad, D.S. Shankar Rao, *Adv. Funct. Mater.* 18 (2008) 1632.
- [34] P.T. Tanev, Y. Liang, T.J. Pinnavaia, *J. Am. Chem. Soc.* 119 (1997) 8616.
- [35] Y. Wan, D.Y. Zhao, *Chem. Rev.* 107 (2007) 2821.
- [36] A. Meister, S. Drescher, I. Mey, M. Wahab, G. Graf, V.M. Garamus, G. Hause, H.-J. Mögel, A. Janshoff, B. Dobner, A. Blume, *J. Phys. Chem. B* 112 (2008) 4506.
- [37] J.B. Huang, G.X. Zhao, *Colloid Polym. Sci.* 273 (1995) 156.
- [38] L. Chen, J.X. Xiao, K. Ruan, J.M. Ma, *Langmuir* 18 (2002) 7250.
- [39] G.X. Zhao, J.X. Xiao, *J. Colloid Interface Sci.* 177 (1996) 513.
- [40] H.Q. Yin, J.B. Huang, M. Mao, H.L. Fu, *Langmuir* 18 (2002) 9198.
- [41] X.R. Zhang, J.B. Huang, M. Mao, S.H. Tang, B.Y. Zhu, *Colloid Polym. Sci.* 279 (2001) 1245.
- [42] H.Q. Yin, Z.K. Zhou, J.B. Huang, R. Zheng, Y.Y. Zhang, *Angew. Chem. Int. Ed.* 42 (2003) 2188.

- [43] H.Q. Yin, J.B. Huang, Y.Y. Lin, Y.Y. Zhang, S.C. Qiu, J.P. Ye, J. Phys. Chem. B 109 (2005) 4104.
- [44] H.Q. Yin, J.B. Huang, Y.Q. Gao, H.L. Fu, Langmuir 21 (2005) 2656.
- [45] H.Q. Yin, S. Lei, S.B. Zhu, J.B. Huang, J.P. Ye, Chem. Eur. J. 12 (2006) 2825.
- [46] E.W. Kaler, A. Kamalakara Murthy, B.E. Rodriguez, J.A.N. Zasadzinski, Science 22 (1989) 1371.
- [47] E.W. Kaler, K.L. Herrington, A.K. Murthy, J.A.N. Zasadzinski, J. Phys. Chem. B 96 (1992) 6698.
- [48] R. Talhout, B.F.N. Engberts, Langmuir 13 (1997) 5001.
- [49] E.F. Marques, O. Regev, A. Khan, M.D. Miguel, B. Lindman, J. Phys. Chem. B 102 (1998) 6746.
- [50] C. Tondre, C. Caillet, Adv. Colloid Interface Sci. 93 (2001) 115.
- [51] S.H. Tang, J.B. Huang, C.Z. Wang, Acta Phys.-Chim. Sin. 18 (2002) 1071.
- [52] J.B. Huang, F. Han, T. Wu, Acta Phys.-Chim. Sin. 19 (2003) 779.
- [53] J.C. Hao, Z.W. Yuan, W.M. Liu, H. Hoffmann, J. Phys. Chem. B 104 (2004) 5105.
- [54] S. Svenson, Curr. Opin. Colloid Interface. Sci. 9 (2004) 201.
- [55] S. Segota, D. Tezak, Adv. Colloid Interface. Sci. 121 (2006) 51.
- [56] R.O. Brito, E.F. Marques, P. Gomes, S. Falcao, O. Soderman, J. Phys. Chem. B 110 (2006) 18158.
- [57] M. Rosa, M.R. Infante, M.da.G. Miguel, B. Lindman, Langmuir 22 (2006) 5588.
- [58] E. Maurer, L. Belloni, T. Zemb, D. Carriere, Langmuir 23 (2007) 6554.
- [59] L.X. Jiang, K. Wang, M.L. Deng, Y.L. Wang, J.B. Huang, Langmuir 24 (2008) 4600.
- [60] E.F. Marques, R.O. Brito, S.G. Silva, J.E. Rodriguez-Borges, M.L. do Vale, P. Gomes, M.J. Araujo, O. Soderman, Langmuir 24 (2008) 11009.
- [61] D. Vivares, E. Soussan, M. Blanzat, I. I. Rico-Lattes, Langmuir 24 (2008) 9260.
- [62] D. Gräbner, L. Zhai, Y. Talmon, J. Schmidt, N. Freiberger, O. Glatter, B. Herzog, H. Hoffmann, J. Phys. Chem. B 112 (2008) 2901.
- [63] Y. Michina, D. Carriere, C. Mariet, M. Moskura, P. Berthault, L. Belloni, T. Zemb, Langmuir 25 (2009) 698.
- [64] S. Bhattacharya, S. De, Langmuir 15 (1995) 3400.
- [65] S. Bhattacharya, S. De, M. Subramanian, J. Org. Chem. 63 (1998) 7640.
- [66] F.P. Hubbard Jr., G. Santonicola, E.W. Kaler, N.L. Abbott, Langmuir 21 (2005) 6131.
- [67] F.P. Hubbard Jr., N.L. Abbott, Langmuir 23 (2007) 4819.
- [68] Y. Yan, J.B. Huang, Z.C. Li, X.L. Zhao, J.M. Ma, Acta Chim. Sin. 60 (2002) 1147.
- [69] Y. Yan, J.B. Huang, Z.C. Li, F. Han, J.M. Ma, Langmuir 19 (2003) 972.
- [70] Y. Yan, J.B. Huang, Z.C. Li, J.M. Ma, H.L. Fu, J. Phys. Chem. B 107 (2003) 1479.
- [71] F. Han, X. He, J.B. Huang, Z.C. Li, Y.L. Wang, H.L. Fu, J. Phys. Chem. B 108 (2004) 5256.
- [72] Y. Yan, W. Xiong, J.B. Huang, Z.C. Li, X.S. Li, N.N. Li, H.L. Fu, J. Phys. Chem. B 109 (2005) 357.
- [73] T. Lu, F. Han, Z.C. Li, J.B. Huang, Langmuir 22 (2006) 2045.
- [74] N. Aydogan, N.L. Abbott, J. Colloid Interface Sci. 242 (2001) 411.
- [75] B.S. Gallardo, K.L. Metcalfe, N.L. Abbott, Langmuir 12 (1996) 4116.
- [76] M.H. Liu, J.F. Cai, Langmuir 16 (2000) 2899.
- [77] A. Meister, M.J. Weygand, G. Brezesinski, A. Kerth, S. Drescher, B. Dobner, A. Blume, Langmuir 23 (2007) 6063.
- [78] G.X. Zhao, Physical Chemistry of Surfactant, Peking University, Beijing, 1991.
- [79] W.A. Zisman, Contact angle, wettability, and adhesion, in: F.M. Fowkes (Ed.), Advances in Chemistry Series, No. 43, ACS, Washington, DC, 1964.
- [80] Y. Yan, J.B. Huang, Z.C. Li, X.L. Zhao, B.Y. Zhu, J.M. Ma, Colloid Surf. A 215 (2003) 263.
- [81] Y. Yan, F. Han, J.B. Huang, Z.C. Li, J.M. Ma, Acta Phys.-Chim. Sin. 18 (2002) 830.
- [82] Y. Yan, S. Guo, W. Xiong, J.B. Huang, Z.C. Li, J.M. Ma, Acta Phys.-Chim. Sin. 21 (2005) 550.
- [83] P. Gao, M.H. Liu, Langmuir 22 (2006) 6727.
- [84] B. Song, G.Q. Liu, R. Xu, S.C. Yin, Z.Q. Wang, X. Zhang, Langmuir 24 (2008) 3734.
- [85] F. Han, J.B. Huang, B. Zheng, Z.C. Li, Colloid Surf. A 242 (2004) 115.
- [86] J.B. Huang, Y. Yan, Z.C. Li, X.L. Zhao, B.Y. Zhu, J.M. Ma, J. Colloid Interface Sci. 258 (2003) 206.
- [87] J.Y. Shin, N.L. Abbott, Langmuir 15 (1999) 4404.
- [88] M. Bonini, D. Berti, J.M. Di Meglio, M. Almgren, J. Teixeira, P. Baglioni, Soft Matter 1 (2005) 444.
- [89] F.P. Hubbard Jr., N.L. Abbott, Soft Matter 4 (2008) 2225.
- [90] S. Bhattacharya, S. De, Chem. Commun. (1996) 1283.
- [91] E. Soussan, A. Pasc-Banu, S. Consola, T. Labrot, E. Perez, M. Blanzat, R. Oda, C. Vidal, I. Rico-Lattes, ChemPhysChem 6 (2005) 2492.
- [92] J.N. Israelachvili, D.J. Mitchell, B.W. Ninham, Biochim. Biophys. Acta 470 (1977) 185.
- [93] J.N. Israelachvili, S. Marcelja, R.G.Q. Horn, Rev. Biophys. 13 (1980) 121.
- [94] G. González-Gaitano, A. Guerrero-Martínez, F. Ortega, G. Tardajos, Langmuir 17 (2001) 1392.
- [95] C. Cabaleiro-Lago, M. Nilsson, A.J.M. Valente, M. Bonini, O. Söderman, J. Colloid Interface Sci. 300 (2006) 782.
- [96] L.X. Jiang, M.L. Deng, Y.L. Wang, D.H. Liang, Y. Yan, J.B. Huang, J. Phys. Chem. B 112, in press.
- [97] T. Lu, F. Han, G.R. Mao, G.F. Lin, J.B. Huang, X. Huang, Y.L. Wang, H.L. Fu, Langmuir 23 (2007) 2932.
- [98] L.I. Jong, N.L. Abbott, Langmuir 16 (2000) 5553.
- [99] B.S. Gallardo, M.J. Hwa, N.L. Abbott, Langmuir 11 (1995) 4209.
- [100] R. Muzzalupo, G. Gente, C. La Mesa, E. Caponetti, D. Chillura-Martino, L. Pedone, M.L. Saladino, Langmuir 22 (2006) 6001.
- [101] G.Z. Mao, Y.H. Tsao, M. Tirrell, H. Ted Davis, V. Hessel, H. Ringsdorf, Langmuir 9 (1993) 3461.
- [102] A. Toutianoush, F. Saremi, B. Tieke, Mater. Sci. Eng. C8–C9 (1999) 343.
- [103] F. Saremi, B. Tieke, Adv. Mater. 10 (1998) 388.
- [104] F. Saremi, G. Lange, B. Tieke, Adv. Mater. 8 (1996) 923.