J. Phys. Chem. B **2005,** *109,* 357−364

Organized Assemblies in Bolaamphiphile/Oppositely Charged Conventional Surfactant Mixed Systems

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Received: August 12, 2004; In Final Form: September 22, 2004

Five ionic bolaamphiphiles were synthesized and the aggregation behavior of bola single systems and bola/oppositely charged conventional surfactant mixed systems was studied. Small spherical vesicles were formed in all these mixed systems revealed by transmission electron microscopy (TEM). Variation of the structure of the hydrophobic chain of bolaamphiphiles has great influences on the vesicle formation ability. Vesicles were also found in the single system of a carboxylate bolaamphiphile, which was attributed to the hydrolysis of the bolaamphiphile.The results of FT-IR and X-ray diffraction (XRD) showed that bolaamphiphiles spanned through the vesicle membranes in these mixed systems. Super thermostability of the vesicles in this kind of mixed system was also investigated.

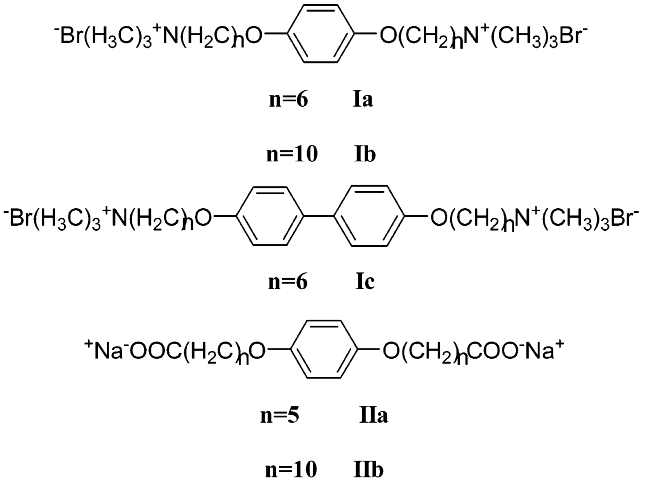
1. Introduction

Vesicles in aqueous solutions have attracted great attention in the past two decades, ranging from fundamental areas in biochemistry and physical chemistry to many applicable aspects, such as pharmacology, catalysis, microreactor, and cosmetics.[1−8] Many studies are focused on the vesiculation of cationic and anionic surfactant mixtures.[9−14] Compared with vesicles prepared from phospholipids or double chain amphiphiles, the catanionic vesicles can form spontaneously and remain stable for a longer time, which takes the big advantage in practical applications.[9,11] To increase the thermostability of catanionic vesicles, one promising way is to develop unconventional surfactants,[15] such as bolaamphiphiles.

Bolaamphiphiles contain a hydrophobic skeleton and two hydrophilic groups on both ends.[16] In the past two decades, some bolaamphiphiles have been synthesized and studied.[17−26] Compared with bilayer membranes formed by conventional surfactants, monolayer membranes are usually formed by bolaamphiphiles based on their special structure. The monolayer membrane systems may provide great convenience for the membrane mimetic investigation due to their stability and fluidity.[24−26] It has been found that the structure of the bolaamphiphiles affects the vesicle formation ability greatly,[21−25] and only micelles were obtained from those with a single hydrocarbon chain.[21,22] Inspired from the catanionic vesicles from conventional single chained cationic and anionic surfactants, catanionic vesicles from bolaamphiphiles with simple structure and oppositely charged conventional surfactants are obviously of great importance. However, so far research in mixed systems containing bolaamphiphiles is still rare.[27]

In our previous work, some interesting results on the special aggregate morphology[28] and super vesicle thermostability[15] have been found in the mixed systems containing bolaamphiphiles. In this study, five new kinds of bolaamphiphiles (Scheme 1) were synthesized with the variation of polar headgroup, hydrocarbon chain length, and introduction of a phenyl group in the molecular structures. The aggregation behavior of these bolaamphiphiles and their mixed systems with oppositely charged conventional surfactants was fully investigated by using TEM (transmission electron microscopy), FT-IR, and XRD (X-ray diffraction). In addition, the thermostability of the vesicles was further studied in the mixed systems.

SCHEME 1: Structure of Bolaamphiphiles



2. Experimental Section

2.1. Materials. Sodium dodecyl sulfate (SDS, 99%) was from Sigma Co. and used as received. Sodium laureate ($C_{11}H_{23}COONa$, abbreviated $C_{11}COONa$) and sodium caprate ($C_9H_{19}COONa$, abbreviated C_9COONa) were prepared by neutralizing the corresponding carboxylic acids with NaOH in ethanol ($C_{11}COOH$ was recrystallized 5 times from an ethanol−water mixed solvent, and C_9COOH was distilled twice to get pure products), then

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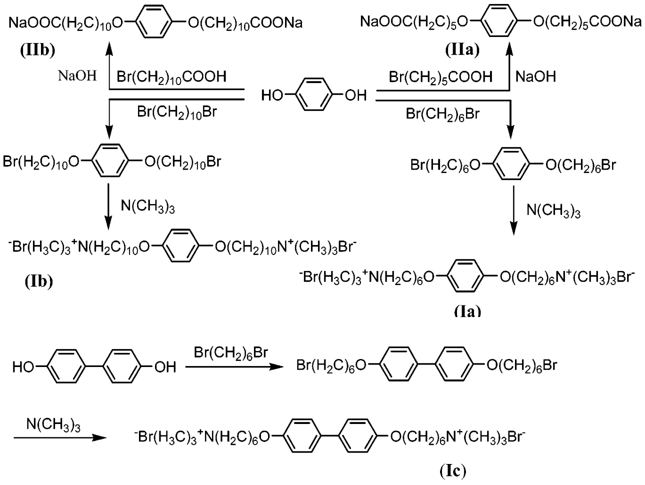
10.1021/jp046365d CCC: $30.25

SCHEME 2: Synthetic Routines for the Preparation of Bolaamphiphiles



the solvents were removed, and the solids were vacuum-dried for 24 h. Dodecyltrimethylammonium bromide (DTAB) and dodecyltriethylammonium bromide (DEAB) were synthesized from dodecyl bromide and trimethylamine or triethylamine, respectively. The crude products were recrystallized five times from ethanol–acetone mixed solvents. The purity of all the surfactants was examined, and no surface tension minimum was found in the surface tension curves. Deionized water was treated with $KMnO_4$ and distilled before use. Other reagents and solvents (A. R. grade) were from Beijing Chemical Co.

2.2. Synthesis of Bolaamphiphiles. Bolaamphiphiles were synthesized as shown in Scheme 2 (see Supporting Information for details).

2.3. Methods. *2.3.1. Surface Tension Measurements.* The surface tension of aqueous surfactant solutions was measured by the drop volume method.[29] The adsorption amount of surfactants was calculated according to the Gibbs adsorption equation:

$$\Gamma_\infty = -\mathrm{d}\gamma/2.303nRT\ \mathrm{d}\log C$$

Here γ is the surface tension in mN m^{-1}, and C is the total concentration of the corresponding surfactant in a system. Γ_∞ is the saturated adsorption amount in mol·m^{-2}. $\{\mathrm{d}\gamma\}/\{\mathrm{d}\log C\}$ is the maximal slope in each case. T is absolute temperature. $R = 8.314$ J mol^{-1} K^{-1}. For a 2:1 electrolyte with no added salt, $n = 3$. For an electrolyte with added salt to keep ionic strength constant, $n = 1$. Then the minimum average area per surfactant molecule (A_{min}) is obtained from the saturated adsorption by

$$A_{\mathrm{min}} = 10^{18}/N_A\Gamma_\infty$$

Here N_A is the Avogadro constant.

The interaction parameter in the micelles was calculated on the basis of Rubingh's equation:[30]

$$\omega_R = \frac{\ln[(X_2\ \mathrm{CMC})/(Y_2\ \mathrm{CMC}_2^0)]}{(1 - Y_2)^2} = \frac{\ln[(1 - X_2)\mathrm{CMC}/(1 - Y_2)\mathrm{CMC}_1^0]}{Y_2^{\ 2}}$$

Here X_2 is the composition of component 2 in the bulk solution, and Y_2 is that in the mixed micelle. CMC, CMC_1^0, and CMC_2^0 are the critical micelle concentration of the mixed solution and the single surfactant solution of components 1 and 2, respectively.

2.3.2. Vesicle Preparation. The catanionic surfactant solutions were prepared by simply mixing the single surfactant stock solutions together. Samples were vortex mixed and equilibrated in a thermostatic bath at 30 °C before the investigation. The mixing ratios are all molar ratio of the two components, and the X_{bola} values refer to the molar fraction of bolaamphiphiles in the mixed systems. The pH values of some solutions were adjusted by Borax to 9.2 and sodium hydroxide to 12.5, respectively.

2.3.3. TEM Measurements. (1) Negative-stained method: uranyl acetate solution (1%, v/v) was used as the staining agent. One drop of the dispersion was placed onto a carbon Formvar-coated copper grid (230 mesh). The excess liquid was sucked away by filter paper. (2) Freeze–fracture technique (FF-TEM): fracturing and replication were carried out in an EE-FED.B freeze–fracture device equipped with a JEE-4X vacuum evaporator. Replicas and negative-stained samples were examined in a JEM-100CX (II) transmission electron microscope.

2.3.4. XRD Measurements. Self-supported cast films for the XRD studies were prepared by dispersing the vesicle suspensions in precleaned glass slides. Reflection XRD studies were carried out with a model XKS-2000 X-ray diffractometer (Scintaginc). The X-ray beam was generated with a Cu anode, and the wavelength of the $K_{\alpha1}$ beam was 1.5406 Å. The X-ray beam was directed toward the film edge, and the scanning was done up to the 2θ value of 10°.

2.3.5. FT-IR Measurements. Vesicle suspensions for FT-IR studies were prepared in D_2O solutions, and then the D_2O solution containing vesicles was placed on a CaF_2 slide for FT-IR examination. The spectra were recorded on a Nicolet Magna-IR 750 Fourier transform spectrometer operating at 4 cm^{-1} resolution.

2.3.6. Fluorescence Probe Measurements. An ethanol solution of pyrene was introduced into the mixed solutions. The ratio of pyrene concentration to the total surfactant concentration was $3.5 \times 10^{-5}/1$. The ethanol volume was less than 1% of the total solution volume (usually the effect of ethanol at this concentration on the surfactant aggregates is insignificant[31,32]). A Hitachi 850 spectrafluorometer was used to determine the micropolarity at various temperatures with an excitation wavelength of 338 nm, an emission wavelength of 350–470 nm, and bandwidths of 5 nm. I_1 and I_3 represent the intensities of the first and the third vibronic peaks in the fluorescence emission spectrum of pyrene.

3. Results and Discussion

3.1. Aggregation Behavior in Cationic Bolaamphiphile/Anionic Conventional Surfactant Systems. *3.1.1. Micellization in Single Cationic Bolaamphiphile Systems and Bolaamphiphile/Conventional Surfactant Catanionic Mixed Systems.* Clear and homogeneous solutions of cationic bolaamphiphiles were obtained by dissolving them (**Ia**, **Ib**, and **Ic**) in water. The surface tension curves of the bolaamphiphiles in water and in 0.1 M NaBr solutions were measured at 30 °C, and some surface-chemical data are listed Table 1. It is found that the CMC values of the bolas in 0.1 M NaBr solutions are smaller than those in aqueous solutions, which is similar to the situation of ionic conventional surfactants. But the CMC values of the bolas are smaller than those of corresponding ionic conventional surfactants, which reveals that the bola have stronger aggregation ability. TEM results based on negative-stained and freeze–

TABLE 1: Surface Properties of Cationic Bola Ia, Ib, and Ic Single Systems (30 °C)

systems	CMC (M)	Γ_∞ (mol m^{-2})	A_{min} (nm^2)
Ia	1.1×10^{-2}	9.99×10^{-7}	1.66
Ib	2.9×10^{-3}	4.52×10^{-7}	3.67
Ic	6.8×10^{-3}	8.99×10^{-7}	1.76
Ia (0.1 M NaBr)	1.1×10^{-3}	2.15×10^{-6}	0.77
Ib (0.1 M NaBr)	6.1×10^{-4}	1.72×10^{-6}	0.97
Ic (0.1 M NaBr)	1.0×10^{-3}	2.52×10^{-6}	0.66

TABLE 2: CMC and γ_{CMC} Values of Cationic Bola (Ia, Ib, and Ic)/Anionic Surfactant Mixed Solutions (X_{bola} = 0.33, 30 °C)

systems	CMC (M)	γ_{CMC} (mN m^{-1})
Ia/SDS	2.5×10^{-4}	33.5
Ia/C_9COONa[a]	3.3×10^{-3}	38.8
Ia/$C_{11}COONa$[a]	2.5×10^{-3}	35.1
Ib/SDS	5.0×10^{-5}	39.4
Ib/C_9COONa[a]	1.4×10^{-3}	37.9
Ib/$C_{11}COONa$[a]	2.0×10^{-4}	36.1
Ic/SDS	4.6×10^{-5}	43.0
Ic/C_9COONa[a]	5.0×10^{-3}	42.7

[a] pH 9.2.

TABLE 3: Vesicles Formed in Cationic Bola/Anionic Conventional Surfactant Mixed Systems

system	C_T (M)	X_{bola}	TEM observation[a]	vesicle diam (nm)
Ia/SDS	1.0×10^{-3}	0.05−0.82	+	10−30
		0.91−1	−	
Ia/C_9COONa[b]	1.0×10^{-2}	0.05−0.82	+	20−40
		0.90−1	−	
Ia/$C_{11}COONa$[b]	1.0×10^{-2}	0.05−0.82	+	20−40
		0.90−1	−	
Ib/SDS	1.0×10^{-4}	0.05−0.91	+	10−50
		1	−	
Ib/C_9COONa[b]	1.0×10^{-3}	0.05−0.90	+	20−50
		1	−	
Ib/$C_{11}COONa$[b]	1.0×10^{-3}	0.05−0.90	+	20−50
		1	−	
Ic/SDS	1.0×10^{-3}	0.05−0.14	−	
		0.33−0.82	+	20−100
		0.90−1	−	
Ic/C_9COONa[b]	1.0×10^{-2}	0.05−0.14	−	
		0.33−0.82	+	10−80
		0.90−1	−	
Ic/$C_{11}COONa$[b]	1.0×10^{-2}	0.05−0.14	−	
		0.33−0.82	+	10−80
		0.90−1	−	

[a] +: vesicles observed. −: no vesicles observed. [b] pH 9.2.

fracture methods showed that no vesicles were formed in such single bola systems, even with the addition of 0.1 M NaBr, indicating that only micelles were formed in these single bola solutions. On the basis of the results of small saturated adsorption amount Γ_∞ and the large minimum average area per surfactant molecule A_{min}, it is indicated that the molecules in the bolaamphiphile aggregates packed loosely, which is in coincidence with the TEM results.

Similar to the situation of conventional cationic and anionic surfactant mixtures, precipitates were easily formed at the electroneutral mixing ratio in cationic bola/anionic conventional surfactant systems. However, homogeneous solutions were obtained at lower concentrations or at other mixing ratios. The CMC values of these mixed systems at a 1:2 mixing ratio (X_{bola} = 0.33) are listed in Table 2. For all the mixed systems above, the CMC values are smaller than both of the two corresponding single systems (the CMC values of SDS, C_9COONa, and $C_{11}COONa$ solutions are 9.7×10^{-3}, 4.2×10^{-2}, and 7.9×10^{-3} M, respectively), which is similar to the case of the conventional catanionic surfactant systems.

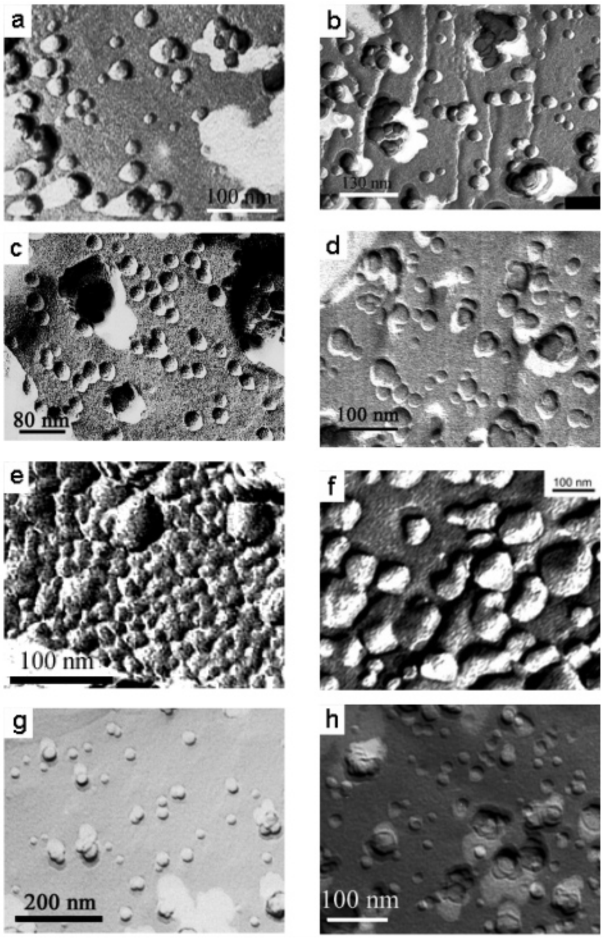


Figure 1. FF-TEM image of vesicles formed in cationic bola/anionic conventional surfactant mixed systems: (a) **Ia**/SDS, $X_{bola} = 0.33$, $C_T = 1.0 \times 10^{-3}$ M; (b) **Ia**/SDS, $X_{bola} = 0.82$, $C_T = 1.0 \times 10^{-3}$ M; (c) **Ia**/C_9COONa, $X_{bola} = 0.83$, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M; (d) **Ib**/SDS, $X_{bola} = 0.91$, $C_T = 1.0 \times 10^{-3}$ M; (e) **Ib**/$C_{11}COONa$, $X_{bola} = 0.60$, pH 9.2, $C_T = 1.0 \times 10^{-3}$ M; (f) **Ic**/SDS, $X_{bola} = 0.60$, $C_T = 1.0 \times 10^{-3}$ M; (g) **Ic**/C_9COONa, $X_{bola} = 0.83$, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M; (h) **Ic**/$C_{11}COONa$, $X_{bola} = 0.83$, pH 9.2, $C_T = 1.0 \times 10^{-3}$ M (C_T is the total surfactant concentration in mixed systems).

3.1.2. Vesicles Formation in Cationic Boaamphiphile/Anionic Conventional Surfactant Mixed Systems. Vesicles are coexisting with micelles in these mixed systems. TEM results revealed the formation of small spherical vesicles with diameters ranging from 10 to 100 nm in **Ia**/SDS, **Ia**/C_9COONa, **Ia**/$C_{11}COONa$, **Ib**/SDS, **Ib**/C_9COONa, **Ib**/$C_{11}COONa$, **Ic**/SDS, **Ic**/C_9COONa, and **Ic**/$C_{11}COONa$ mixed systems, and these vesicles were stable in solutions with or without 0.05 M NaBr for six months. The vesicle formation results in these mixed systems are shown in Figure 1 and Table 3.

From Table 3 we can find that the variation of the cationic bolas' structure influences the vesicle formation ability in these mixed systems. Increase of phenyl group in the center of bolas is disadvantageous to the vesicle formation. To draw a comparison between two series of mixed systems of **Ia**/anionic conventional surfactant and **Ic**/anionic conventional surfactant, the mixing ratio ranges for the vesicle formation are in the following order:

$$\textbf{Ia}/\mathrm{SDS} > \textbf{Ic}/\mathrm{SDS};\quad \textbf{Ia}/\mathrm{C_9COONa} > \textbf{Ic}/\mathrm{C_9COONa};\quad \textbf{Ia}/\mathrm{C_{11}COONa} > \textbf{Ic}/\mathrm{C_{11}COONa}$$

The increase of the hydrophobic chain length is in favor of vesicle formation in mixed systems due to the hydrophobic

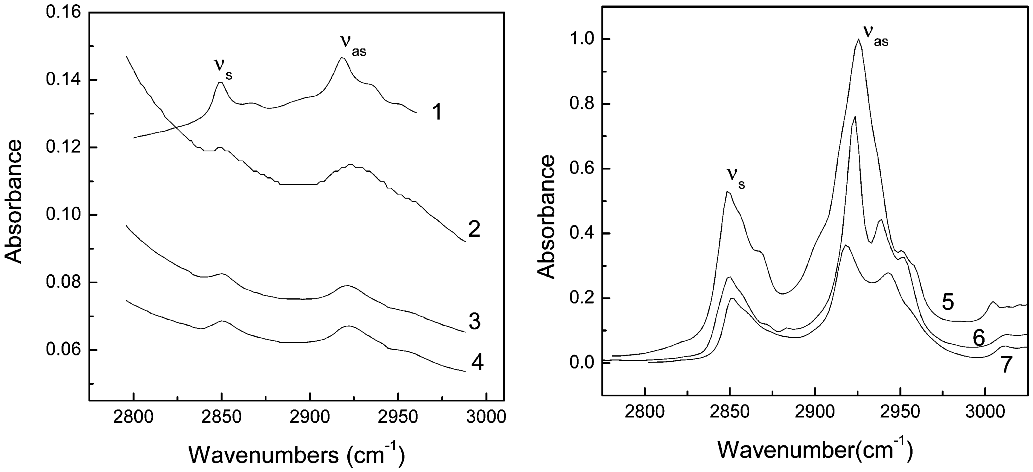


Figure 2. ν_{as} and ν_s of the CH_2 group in cationic bola/anionic conventional surfactant mixed systems: (1) **Ib**/SDS; (2) **Ia**/SDS; (3) **Ia**/C_{11}COONa; (4) **Ia**/C_9COONa; (5) **Ib**/C_9COONa; (6) **Ic**/C_{11}COONa; (7) **Ic**/SDS.

effect. **Ib**/anionic conventional surfactant mixed systems have a broader mixing ratio range and lower total surfactant concentration, necessary for vesicle formation, than that of **Ia**/anionic conventional surfactant mixed systems. In addition, the nature of the anionic conventional surfactants also affects the concentration range for vesicle formation in the mixed systems. It is clear that in bola/SDS mixed systems, the concentration for vesicle formation is about $10^{-4}-10^{-3}$ M, while in bola/C_9COONa or C_{11}COONa mixed systems, the concentration would be as higher as $10^{-3}-10^{-2}$ M. The stronger interaction between cationic bolas and SDS than that between cationic bolas and C_9COONa or C_{11}COONa may be responsible for this phenomenon. It is found that the interaction parameter (ω_R) values in **Ib**/SDS and **Ib**/C_{11}COONa mixed systems are -10.9 and -7.2 (the CMC values of SDS, C_{11}COONa, **Ib**/SDS, and **Ib**/C_{11}COONa solutions with 0.1 M NaBr are 3.6×10^{-3}, 9.6×10^{-3}, 1.0×10^{-4}, and 1.2×10^{-4} M, respectively), which indicates that the interaction between **Ib** and SDS is stronger than that between **Ib** and C_{11}COONa. However, an increase of the chain length of alkyl carbonate, such as from C_9COONa to C_{11}COONa, has no obvious effect on the vesicle formation capability.

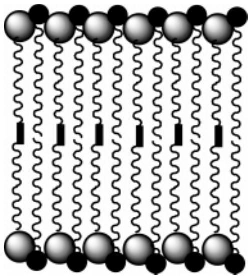
FT-IR spectra of the vesicle solutions were measured to obtain further insights into structural properties of the intramolecular chain conformation and intermolecular chain packing of the membrane-forming amphiphiles. It is known that the CH_2 vibration is sensitive to the order of molecular packing.[33-35] The CH_2 asymmetric (υ_{as}) and symmetric stretching (υ_s) vibration bands usually shift from 2929 to 2920 cm^{-1} and 2856 to 2850 cm^{-1}, respectively, when the molecular packing turns from a disordered state to a highly ordered one. Typical FT-IR spectra in the mixed systems are shown in Figure 2. It is clear that the wavenumber of the above two bands appeared near 2921 and 2850 cm^{-1}, respectively, in each system (see Table 4), which indicates that the methylene chains stretch in the membrane, taking the highly ordered states with preferential all-trans conformations.[33-35]

TABLE 4: FT-IR (ν_{as} and ν_s of CH_2 Group) Results in Cationic Bola/Anionic Conventional Surfactant Mixed Systems

mixed systems	X_{bola}	ν_{as} (cm^{-1})	ν_s (cm^{-1})
Ia/SDS	0.33	2922	2850
Ia/C_9COONa[a]	0.33	2921	2851
Ia/C_{11}COONa[a]	0.33	2920	2849
Ib/SDS	0.60	2919	2849
Ib/C_9COONa[a]	0.60	2925	2849
Ic/SDS	0.60	2918	2851
Ic/C_{11}COONa[a]	0.60	2923	2850

[a] pH 9.2.

SCHEME 3: Illustration of Molecular Arrangement in Mixed Surfactant Vesicle Membranes



XRD is a powerful method for elucidating long-range structures of ordered molecular assemblies. It has been demonstrated that the self-aggregate structure of amphiphiles is well preserved in the cast films.[36-38] To obtain the organized structure of the assemblies in aqueous solution, the small-angle XRD method is used to study the long-range organized structure of the cast membranes. The representative XRD patterns of cast films for dispersions **Ia**/SDS, **Ib**/SDS, **Ic**/SDS, and **Ic**/C_9COONa are illustrated in Figure 3. It can be seen that the samples exhibit periodic peaks corresponding to the thickness of the membranes, which is similar to those reported in other amphiphiles' cast films. According to the Bragg equation, the layer spacings for **Ia**/SDS, **Ib**/SDS, **Ic**/SDS, and **Ic**/C_9COONa are calculated to be 3.8, 3.9, 3.8, and 2.7 nm, respectively. The molecular lengths of **Ia**, **Ib**, **Ic**, SDS, and C_9COONa are estimated to be about 2.6, 3.1, 3.5, 1.8, and 1.3 nm, respectively, from the ChemBats3D Modeling. It is clear that the thickness of vesicle membranes is close to the molecular length of bolaamphiphiles and about twice the molecular length of corresponding conventional anionic surfactant. Combining the above FT-IR results that the bolaamphiphiles stretch through the membrane, it is clear that **Ia**, **Ib**, and **Ic** are spanning in the membrane to form the skeleton of vesicles. The proposed molecular packing modes based on the FT-IR and XRD results in the catanionic membrane are illustrated in Scheme 3.

3.2. Aggregation Behavior in Anionic Bolaamphiphile/Cationic Conventional Surfactant Mixed Systems. *3.2.1. Aggregate Formation in Anionic Bolaamphiphile Systems.* Anionic bolaamphiphiles **IIa** can be dissolved in water (pH 9.2) at room temperature below 5.0×10^{-2} M. However, it is

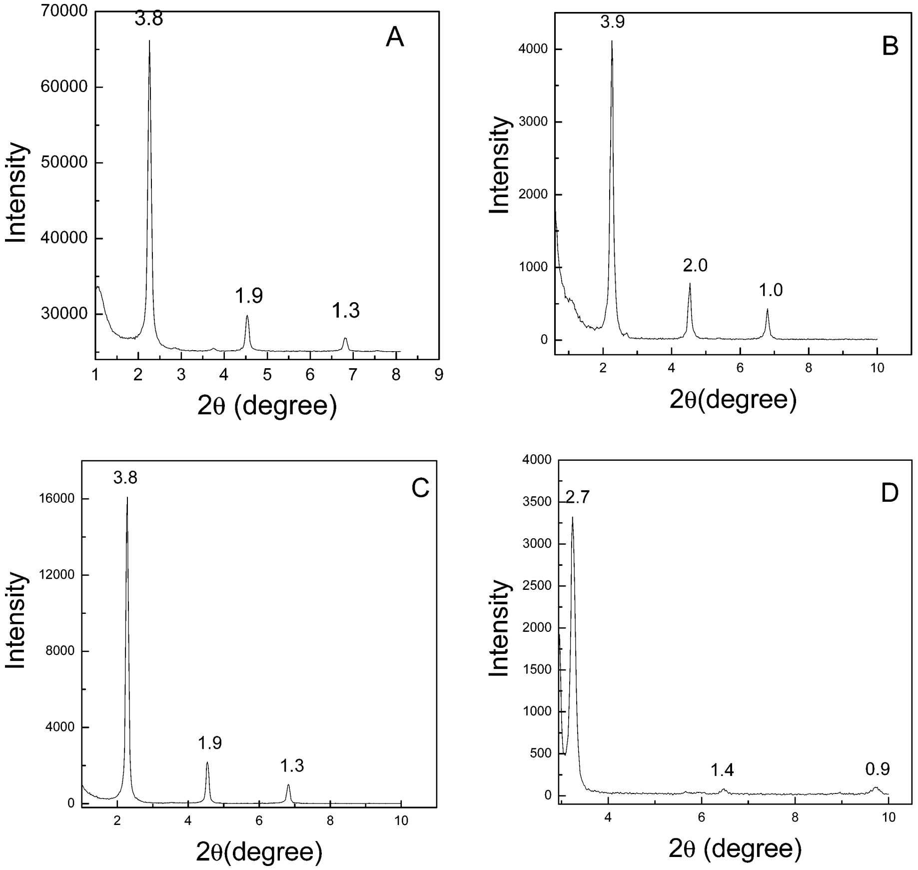


Figure 3. XRD diagrams of some mixed systems ($X_{bola} = 0.60$): A) **Ia**/SDS, $C_T = 1.0 \times 10^{-3}$ M; (B) **Ib**/SDS, $C_T = 1.0 \times 10^{-4}$M; (C) **Ic**/SDS, $C_T = 1.0 \times 10^{-3}$ M; (D) **Ic**/C_9COONa, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M.

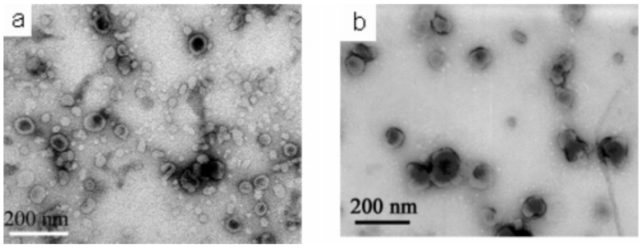


Figure 4. Negative-stained TEM images of vesicles in (a) a **IIa** single system (pH 9.2, [**IIa**] = 1.0×10^{-2} M) and (b) a **IIa**/n-C_8OH mixed solution (pH 12.5, [**IIa**] = 1.0×10^{-2} M, [n-C_8OH] = 3.0×10^{-4} M).

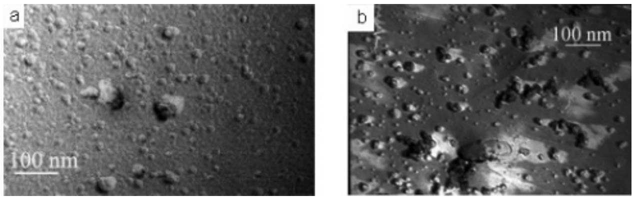


Figure 5. FF-TEM images of vesicles induced by the addition of long-chain alcohol: (a) [**Ia**] = 1.0×10^{-2} M, [n-C_8OH] = 3.8×10^{-3} M; (b) [**Ic**] = 1.0×10^{-2} M, [n-$C_{12}OH$] = 8.8×10^{-3} M.

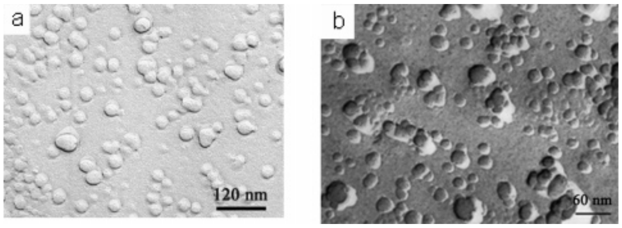


Figure 6. FF-TEM image of vesicles in a **IIa**/DTAB mixed system ($X_{bola} = 0.33$, $C_T = 1.0 \times 10^{-2}$ M): (a) pH 9.2; (b) pH 12.5.

difficult for **IIb** to dissolve in water under the same conditions. TEM observations revealed vesicles with diameters of 20−100 nm in **IIa** solution at pH 9.2 (Figure 4a). This is a novel result since it is usually thought that vesicles are easily formed by double-chained[39] bolaamphiphiles and micelles by those single-chained bolaamphiphiles. The vesicle formation in **IIa** solution may be attributed to the following equilibrium:

$$^{-}OOC(CH_2)_5OPhO(CH_2)COO^{-} + 2H_2O \rightleftharpoons HOOC(CH_2)_5OPhO(CH_2)COOH + 2OH^{-}$$

Therefore, the **IIa** system is the mixture of bola-form alkyl free acid and its sodium salt. Although the acid form is a little in solution at pH 9.2, it will be enriched in the aggregates due to the hydrophobic effect. According to the geometry rule,[40] the critical molecular packing parameter is given by $P = V_c/a_0l_c$, 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 of 0.5−1, while for micelle formation $P <$ 0.5. The bola-form alkyl free acid in the aggregates will reduce the electrostatic repulsion between the headgroups of **IIa**, i.e., decrease a_0. Therefore the value of P will increase, and accordingly, vesicles can form in **IIa** solution. On the basis of this assumption, the decrease of the acid form in this system will destroy the formation of vesicles. By increasing the pH of the **IIa** solution to 12.5, the ratio of free acid to its sodium salt will decrease greatly as that in pH 9.2. As expected, no vesicles were observed in the pH 12.5 solution. However, vesicles could be observed again when a small amount of octanol was added

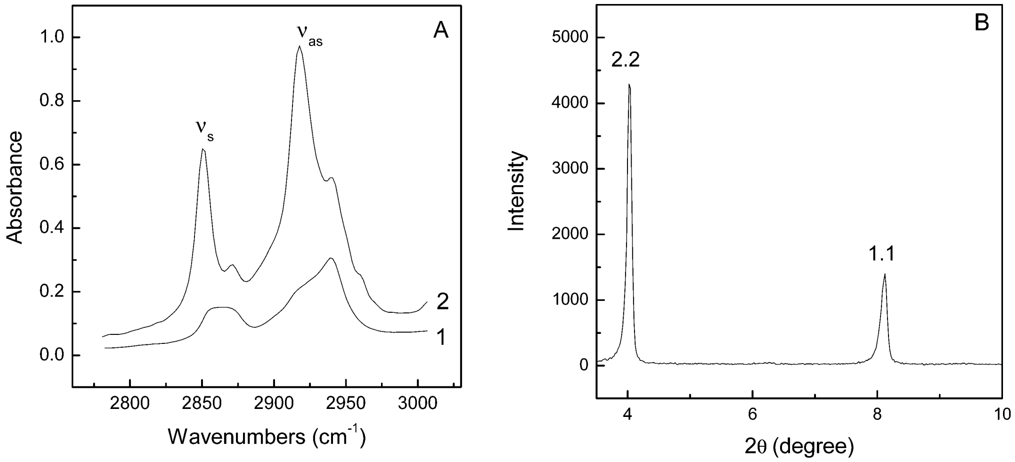


Figure 7. (A) ν_{as} and ν_s of CH_2 group in (1) a **IIa** single system (pH 9.2, 1.0×10^{-2} M) and (2) a **IIa**/DTAB mixed system ($X_{bola} = 0.33$, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M). (B) XRD diagrams in a **IIa**/DTAB mixed system ($X_{bola} = 0.33$, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M).

TABLE 5: Vesicle Formation in the IIa/DTAB Mixed System ($C_T = 1.0 \times 10^{-2}$ M)

X_{bola}	pH 9.2[a]	pH 12.5[a]
0	−	−
0.14	+	+
0.33	+	+
0.60	+	+
1	+	−

[a] +: vesicles observed by TEM. −: no vesicles observed by TEM.

TABLE 6: FT-IR (ν_{as} and ν_s of CH_2 Group) and XRD (d) Results of the IIa (pH 9.2, 1.0×10^{-2} M) and IIa/DTAB Systems ($X_{bola} = 0.33$, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M)

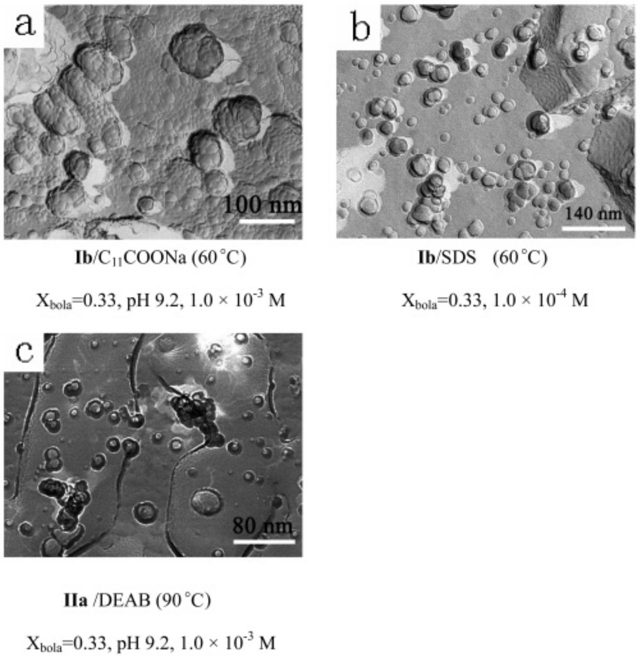
systems	ν_{as} (cm^{-1})	ν_s (cm^{-1})	d (nm)
IIa/DTAB	2918	2851	2.2
IIa	2940	2865	2.1

to the **IIa** solution at pH 12.5 (Figure 4b). Moreover, vesicles were also observed when alkyl alcohol was added in the cationic bola **Ia**, **Ib**, or **Ic** single systems, respectively (Figure 5). These results demonstrate the importance of the tiny amount of polar organic compounds (alkyl alcohol or acid) for vesicle formation (Hoffmann and co-workers have extensively studied the contribution of alkyl alcohol to the phase behavior of surfactant systems[41]).

*3.2.2. Vesicle Formation in **IIa**/Cationic Conventional Surfactant Mixed Systems.* At room temperature, clear and homogeneous solutions of **IIa**/DTAB could be obtained. TEM images illustrated that vesicles existed in **IIa**/DTAB mixed systems of different mixing ratio at not only pH 9.2 but also pH 12.5 with the diameter of 30−100 and 50−200 nm (Figure 6), respectively, indicating that the addition of DTAB is helpful to the vesicle formation in this bola's system. Some TEM results are listed in Table 5. A similar situation of vesicle formation was also observed in the **IIa**/DEAB mixed system.

The packing of hydrocarbon chains of surfactant molecules in the **IIa**/DTAB mixed system was investigated by FT-IR. The results are shown in Figure 7A and Table 6. It is clear that the wavenumber of the CH_2 vibration appeared lower than that of the **IIa** single system, which indicates that molecules in the **IIa**/DTAB mixed system pack denser than in the **IIa** single system and the alkyl chains are in a highly ordered state. This can be accredited to the strong electrostatic attraction which pulls the hydrophobic chain closer in the **IIa**/DTAB mixed system.

The long-range organized structure of the cast film for **IIa**/DTAB mixed vesicles was examined. It can be seen from Figure 7B that the mixed systems exhibit periodic peaks corresponding to the thickness of the membranes, which is similar to those cationic bola/anionic surfactant systems. According to the Bragg equation, the layer spacing is calculated to be 2.2 nm, which is similar to the length of **IIa** (2.1 nm, the XRD results of **IIa** and ChemBats3D modeling give the same results). This result indicates that **IIa** molecules take the stretching conformation through the vesicle membranes in the mixed systems, which is similar to the packing mode in the **Ia**/SDS mixed system.



Ib/C_{11}COONa (60 °C)

X_{bola}=0.33, pH 9.2, 1.0×10^{-3} M

Ib/SDS (60 °C)

X_{bola}=0.33, 1.0×10^{-4} M

IIa /DEAB (90 °C)

X_{bola}=0.33, pH 9.2, 1.0×10^{-3} M

Figure 8. FF-TEM images of vesicles formed in different bola/oppositely charged conventional surfactant mixed systems.

3.3. Thermostability of Vesicles in Bolaamphiphile/Oppositely Charged Conventional Surfactant Mixed Systems.

3.3.1. TEM Observation. In previous reports, we have discovered superior thermostability of vesicles in the synthetic bolaamphiphiles sodium eicosanedioate ($NaOOC(CH_2)_{18}COONa$, or SEDA) and conventional cationic surfactant DEAB mixed system.[15] In this article, we systematically investigated the thermostability of vesicles in bolaamphiphile/oppositely charged conventional surfactant mixed systems. The TEM results revealed that the vesicles in cationic bola/C_{11}COONa mixed systems became fused at ~60 °C (Figure 8a), while those in cationic bola/SDS mixed systems were still stable at this temperature (Figure 8b). In addition, vesicles in anionic bola/

TABLE 7: TEM Observation of Vesicle Formation in Bola/Oppositely Charged Conventional Surfactant Mixed Catanionic Systems at Different Temperatures

	25 °C[a]	40 °C[a]	60 °C[a]	90 °C[a]
Ia/SDS	+	+	+	+
Ia/C_9COONa	+	+	fusion	
Ia/C_{11}COONa	+	+	fusion	
Ib/SDS	+	+	+	+
Ib/C_9COONa	+	+	fusion	
Ib/C_{11}COONa	+	+	fusion	
Ic/SDS	+	+	+	+
Ic/C_9COONa	+	+	fusion	
Ic/C_{11}COONa	+	+	fusion	
IIa/DTAB	+	+	+	+
IIa/DEAB	+	+	+	+

[a] +: vesicles exist in the system.

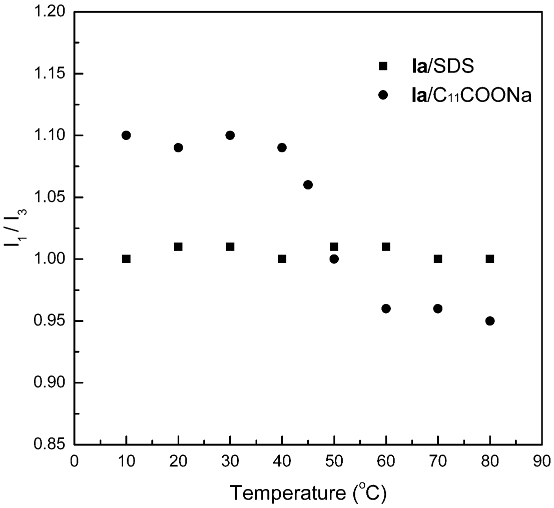


Figure 9. I_1/I_3 of **Ia**/SDS and **Ia**/C_{11}COONa systems at different temperatures (**Ia**/SDS, $C_T = 1.0 \times 10^{-3}$ M, [pyrene] $= 3.5 \times 10^{-8}$ M; **Ia**/C_{11}COONa, pH 9.2, $C_T = 1.0 \times 10^{-2}$ M, [pyrene] $= 3.5 \times 10^{-7}$ M).

DTAB and anionic bola/DEAB mixed systems still existed even when the temperature reached ~90 °C (Figure 8c), although the size of the vesicles became heterogeneous. The TEM results are listed in Table 7.

3.3.2. Fluorescence Results. To further investigate the thermostability of vesicles observed from TEM, the vibrational intensity ratio I_1/I_3 of a hydrophobic fluorescence probe, pyrene,[42] in the mixed systems at different temperatures was also studied. Figure 9 shows the dependence of the I_1/I_3 ratio on the temperature in the **Ia**/SDS and **Ia**/C_{11}COONa systems. It is clear that the I_1/I_3 value in the **Ia**/C_{11}COONa system sharply decreased when the temperature reached 40−50 °C, and then became constant with further increase in temperature. Therefore, the phase transition temperature of the membrane bilayers in this kind of system can be estimated in the range of 40−50 °C, which is in coincidence with the result of the TEM observations. However, the I_1/I_3 values versus temperature in the **Ia**/SDS system did not change obviously, suggesting that no phase transition occurred in the whole experimental temperature range (20−90 °C). This result agrees well with the TEM observations. The fluorescence probe measurements in other bola/conventional surfactant mixed systems cannot be performed, since the fluorescence was quenched in those systems.

The above results suggested that it is a general phenomenon that the vesicles in bolaamphiphile/oppositely charged conventional surfactant mixed systems are of super thermostability. It is interesting to find that the vesicles in the cationic bola/anionic surfactant mixed systems are closely related to the structure of anionic surfactant, for example, the thermostability of vesicles formed in the bola/SDS mixed systems is superior to that in the bola/C_{11}COONa mixed systems, which may be attributed to the electrostatic interaction between the headgroups in the former being stronger than that in the latter. It is also notable that vesicles in the anionic bola/cationic conventional surfactant mixed systems (**IIa**/DTAB and **IIa**/DEAB) are more stable against temperature than those in the cationic bola/anionic conventional surfactant systems (**Ia**/C_mCOONa, $m = 9$ or 11) although the headgroups in these mixed systems are the same, which suggests that the vesicle membrane stability is not only controlled by the electrostatic interaction between the headgroups but also ruled by a comprehensive interaction between the hydrophobic chains.

4. Conclusions

Vesicles were formed in all bolaamphiphile/oppositely charged conventional surfactant mixed systems. Compared to single bola systems, the mixed systems display super vesicle formation capability and stability. Decreasing the phenyl group and increasing the hydrocarbon chain of cationic bolas can help the vesicle formation in the mixed systems. The variation of oppositely charged conventional surfactants also has an effect on vesicle formation. All the bolaamphiphiles adopt a stretching conformation in vesicle membranes. It is found that the super thermostability of vesicles in the mixed bola and oppositely charged conventional surfactant systems is mainly due to the special stretching conformation of the hydrocarbon chain in bolas and the strong electrostatic interaction between the headgroups of bolas and oppositely charged conventional surfactants. We hope this work may provide further insights into the nature of vesicle formation in bola/oppositely charged conventional surfactant mixed systems and help to make stable vesicles based on bola-form amphiphiles which may shed light on material preparation based on vesicle application as microreactor.

Acknowledgment. The project was supported by the National Natural Science Foundation of China (20233010, 20373003, 20425310).

Supporting Information Available: Experimental details for the synthesis of bolaamphiphiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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