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Aggregates Transition Depending on the Concentration in the Cationic Bolaamphiphile/SDS Mixed Systems

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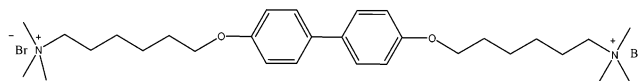
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1. Introduction

Bolaamphiphiles are amphiphiles with two headgroups connected by one or two hydrocarbon chains. In the last two decades, bolaamphiphiles have drawn much attention^{1,2} due to their superior capability in monolayer membrane (MLM) formation^{3,4} and biomembrane simulation.⁵ Many efforts were made to design and synthesize bola molecules with different structures,^{6,7} as well as to characterize their aggregation behaviors in aqueous solution.^{8,9} Usually, bolaamphiphiles with double hydrocarbon chains can form globular vesicles in aqueous solution.¹⁰ Recent studies showed that some single chain bolaamphiphiles could also form vesicles.^{11,12} Moreover, tubelike vesicles¹³ and fibrous¹⁴ and helical structures¹⁵ have been found in some aqueous solutions of bolaamphiphiles.

Compared with single bolaamphiphile systems, the mixed systems of bola and conventional surfactants also caught the eyes of some researchers. Bhattacharya et al.^{16,17} reported the vesicle formation from hybrid bolaamphiphile/amphiphile ion pairs. Other reports on the mixed systems of bolaamphiphile/amphiphile mainly focused on the neutral molecules¹⁸ or molecules with the same kind of charge.¹⁹ However, compared with the numerous works on the single system of bolaamphiphiles, rare are the studies on the mixed systems of bolaam-

Chart 1. Structure of $N^+-C_6-BP-C_6-N^+$



phiphile/oppositely charged conventional surfactants. It is well-known that the mixture of conventional catanionic surfactant systems will provide bilayer type aggregates (vesicles and so forth) easily.^{20,21} Therefore, it is prospective to probe the aggregation behavior in the catanionic bolaamphiphile/conventional amphiphile mixed systems. In this work, we reported the transition of different types of aggregate which depended on the concentration of aqueous biphenyl-4,4'-bis(oxyhexyltrimethylammonium bromide) ($N^+-C_6-BP-C_6-N^+$; Chart 1)/SDS solutions.

2. Experimental Section

Materials. The bolaamphiphile ($N^+-C_6-BP-C_6-N^+$) was synthesized in this laboratory (see Supporting Information). Sodium dodecyl sulfate (SDS, 99%) was from Sigma Co. and used as received. Dimethyl yellow, bromophenol blue, and other reagents were all Beijing Chemical Co. products of analytical grade.

Methods. The catanionic surfactant solutions were prepared by weighing cationic bolaamphiphile ($N^+-C_6-BP-C_6-N^+$) and water first in the sample vial (allowing the bolaamphiphile to dissolve) and then adding an SDS stock solution of desired concentration. Samples were vortex mixed after the vials were sealed, and samples were equilibrated in a thermostatic bath at 30 °C for over 3 weeks before investigation.

Samples for electron microscopy were prepared by the freeze-fracture technique. Fracturing and replication were carried out in a high-vacuum freeze-etching system (Balzers BAF-400D). Replicas were examined in a JEM-200CX transmission electron microscope. The surface tension was measured by the drop volume method.²² The measurement of the UV-vis spectra was performed with a Shimadzu UV-250 spectrophotometer (1 cm quartz cell).

3. Results and Discussion

At room temperature (~25 °C), clear and homogeneous solutions of mixed ($N^+-C_6-BP-C_6-N^+$)/SDS systems could be obtained when the total surfactant concentration (C_{total}) was equal to or less than 1.0×10^{-3} mol/L even at the 1:2 mixed molar ratio (the electroneutral mixing ratio). Transmission electron microscopy (TEM) analysis of the mixed $N^+-C_6-BP-C_6-N^+$ /SDS solution (25 °C, $C_{total} = 1.0 \times 10^{-3}$ mol/L, molar ratio 1:2, 3:2, 9:2) revealed the presence of dispersed vesicles (Figure 1a and b). However, no vesicles were found in the mixed systems of ($N^+-C_6-BP-C_6-N^+$)/SDS ratio less than 1:2. When the vesicular solutions were diluted to 1.0×10^{-4} mol/L (10 times dilution), the vesicles disappeared and large elongated molecular aggregates with a width of about 10–20 nm were observed (Figure 1c and d). In all three systems, these elongated aggregates branched and connected with each other to form networks although the morphology of the elongated aggregates showed a little variation with the changing of mixing ratio. Similar elongated aggregates were found in the 4-butylazobenzene-4-(oxyethyl)trimethylammonium bromide (AZTMA)/SDS mixtures by Hideki Sakai et al.²³ when the AZTMA molecules were

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- (1) Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1937.
- (2) Hentrich, F.; Tschierske, C.; Diele, S.; Sauer, C. *J. Mater. Chem.* **1994**, *4*, 1547.
- (3) Meguro, K.; Ikeda, K.; Otsuji, A.; Yasuda, M.; Esumi, K. *J. Colloid Interface Sci.* **1987**, *118*, 372.
- (4) Mackenzie, K. C.; Bunton, C. A.; Nicoli, D. F.; Saelli, G. *J. Phys. Chem. B* **1987**, *91*, 5709.
- (5) Yiv, S.; Kale, K.; Lang, M.; Zana, R. *J. Phys. Chem. B* **1976**, *80*, 2651.
- (6) Okahata, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1979**, *101*, 5231.
- (7) Fuhrhop, J. H.; Mathieu, J. *J. Chem. Soc., Chem. Commun.* **1983**, 144.
- (8) Heiser, U. F.; Dobner, B. *Chem. Commun.* **1996**, 2025.
- (9) Kunitake, T.; Tsuge, A.; Takarabe, K. *Polym. J.* **1985**, *17*, 633–640.
- (10) Fuhrhop, J. H.; Fritsch, D. *Acc. Chem. Res.* **1986**, *19*, 130.
- (11) Meglia, C. D.; Rananavare, S. B.; Svenson, S.; Thompson, D. H. *Langmuir* **2000**, *16*, 128.
- (12) Clary, L.; Gadras, C.; Greiner, J.; Rolland, J.-P.; Santaella, C.; Vierling, P.; Gulik, A. *Chem. Phys. Lipids* **1999**, *99*, 125.
- (13) Fuhrhop, J. H.; Spiroski, D.; Boettcher, C. *J. Am. Chem. Soc.* **1993**, *115*, 1600.
- (14) Franceschi, S.; Viguerie, N. de; Riviere, M.; Lattes, A. *New J. Chem.* **1999**, *23*, 447.
- (15) Nakashima, N.; Asakuma, S.; Kim, J. M.; Kunitake, T. *Chem. Lett.* **1984**, 1709.
- (16) Bhattacharya, S.; De, S. *Chem. Commun.* **1996**, 1283.
- (17) Bhattacharya, S.; De, S.; Subramanian, M. *J. Org. Chem.* **1998**, *63*, 7460.
- (18) Visscher, I.; Engberts, J. B. F. N. *Langmuir* **2000**, *16*, 52.
- (19) Zana, R.; Muto, Y.; Esumi, K.; Meguro, K. *J. Colloid Interface Sci.* **1988**, *123*, 502.

(20) Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. N. *Science* **1989**, *245*, 1371.

(21) Zhao, G.-X.; Huang, J. B. *Acta Phys.-Chim. Sci.* **1992**, *8*, 533.

(22) Moss, R. A.; Fujita, T.; Okumura, Y.; Lang, T.; Abe, M. *J. Phys. Chem. B* **1999**, *103*, 10737.

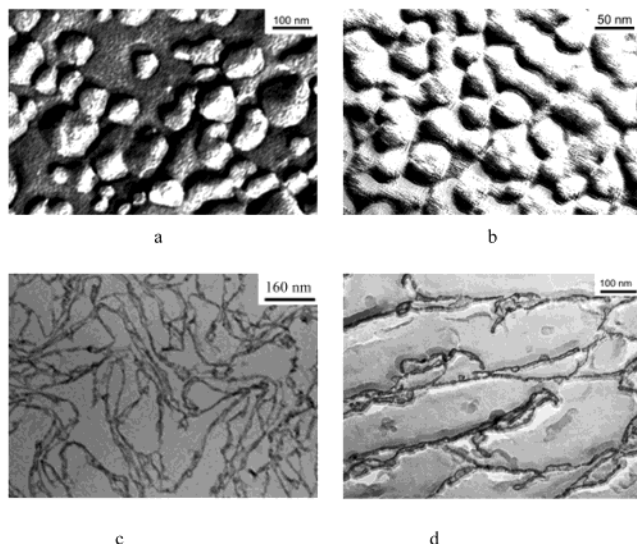


Figure 1. Freeze replica TEM micrographs for aqueous ($N^+-C_6-BP-C_6-N^+$)/SDS mixed solutions. $[NaBr] = 0.1$ mol/L: (a) ($N^+-C_6-BP-C_6-N^+$), SDS = 1:2, $C_{total} = 1.0 \times 10^{-3}$ mol/L; (b) ($N^+-C_6-BP-C_6-N^+$), SDS = 9:2, $C_{total} = 1.0 \times 10^{-3}$ mol/L; (c) ($N^+-C_6-BP-C_6-N^+$), SDS = 1:2, $C_{total} = 5 \times 10^{-5}$ mol/L; (d) ($N^+-C_6-BP-C_6-N^+$), SDS = 3:2, $C_{total} = 6.0 \times 10^{-5}$ mol/L.

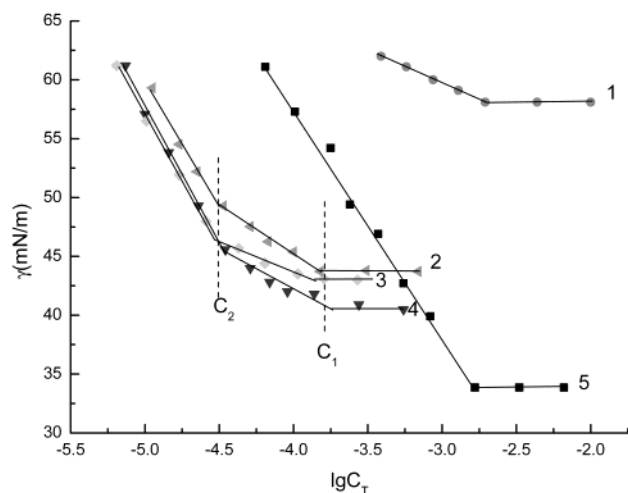


Figure 2. Surface tension curves of ($N^+-C_6-BP-C_6-N^+$)/SDS mixed systems (30 °C, $[NaBr] = 0.1$ mol/L). The mixing ratios [$N^+-C_6-BP-C_6-N^+$]:SDS were as follows: (1) 1:0; (2) 9:2; (3) 3:2; (4) 1:2; (5). 0:1.

irradiated by UV light. However, the nature of these elongated aggregates was still not clear.²³ Further dilution of these solutions to 1.0×10^{-5} mol/L (100 times dilution) lead to the disappearance of these elongated aggregates.

Interestingly, two transition points were found in the surface tension curves of these mixed aqueous solutions (Figure 2). Usually only one break will be expected in those of conventional surfactant systems. When the concentration reaches the break point, micelles start forming or vesicles and micelles start coexisting^{24,25} in the solution. There were also some cases where two breaks coexist in the surface tension curves of some bolaamphiphiles. This phenomenon was usually attributed to the coexistence of different sorts of micelles²⁶ in this kind of system. In our experiments, vesicles only existed at the

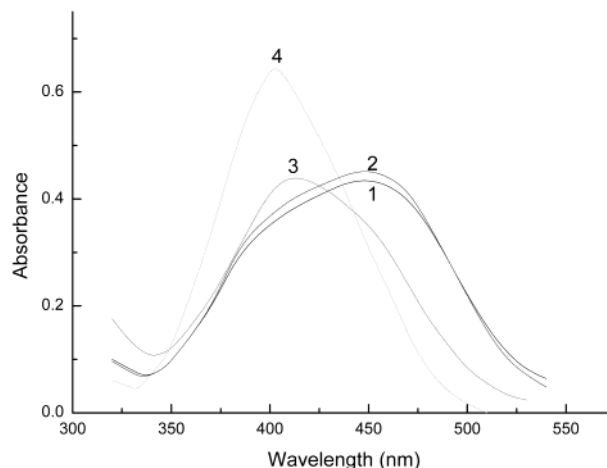


Figure 3. UV-vis spectra of dimethyl yellow in different systems: (1) 0.1 mol/L NaBr aqueous solution; (2 and 3) aqueous solutions of ($N^+-C_6-BP-C_6-N^+$)/SDS = 3:2, $[NaBr] = 0.1$ mol/L, total surfactant concentration 5.0×10^{-5} mol/L (2) or 1.0×10^{-3} mol/L (3); (4) ethanol.

Table 1. Concentrations Corresponding to the Two Break Points in the Surface Tension Curves of the Mixed ($N^+-C_6-BP-C_6-N^+$)/SDS Solutions

mixing ratio	$10^4 C_1$ (mol/L)	$10^5 C_2$ (mol/L)
1:2	1.35	2.88
3:2	1.78	3.47
9:2	1.55	3.09

concentration corresponding to the horizontal part of the curve, while the elongated aggregates exist between the two breaks (The concentrations corresponding to the two breaks, C_1 and C_2 , are listed in Table 1 and marked in Figure 2). This result indicated that the aggregation behavior of the mixed ($N^+-C_6-BP-C_6-N^+$)/SDS solution was highly dependent on the mixed surfactant concentration.

The dye solubilization and entrapment experiments were also conducted to identify the nature of these large molecular aggregates. Neutral and water insoluble dimethyl yellow was used as the probe, since it would have less effect on the electrostatic interaction in the catanionic surfactant system. A 30 μ L ethanol solution of 0.04% (wt) dimethyl yellow was added into 3 mL of water, and the maximum absorption of dimethyl yellow appeared at 450 nm. However, in the 1.0×10^{-3} mol/L catanionic surfactant solution and in pure ethanol, the maximum absorbance moved to 410 nm. It is well-known that the UV spectra of the chromophore are related to the polarity of the solvent.²⁷ The polarity of the aqueous solution is bigger than that in the core of micelles.^{28,29} Accordingly, the polarity of the molecular membrane of the ($N^+-C_6-BP-C_6-N^+$)/SDS mixture will also be lower than that of the aqueous solution. Shown in Figure 3 are the UV spectra of dimethyl yellow in different systems. It can be seen that an obvious blue shift of dimethyl yellow occurred in the 1.0×10^{-3} mol/L 3:2 system. A similar phenomenon was also observed in the 1:2 and 9:2 systems. The remarkable blue shift of dimethyl yellow in ($N^+-C_6-BP-C_6-N^+$)/SDS mixed aqueous solution suggests that the dye molecules locate in the hydrophobic area of the vesicle

(23) Mao, M.; Huang, J. B.; Zhu, B. Y.; Ye, J. P. *J. Phys. Chem. B* **2002**, *106*, 219.

(24) Sakai, H.; Matsumura, A.; Yokoyama, S. *Langmuir* **1991**, *7*, 24.

(25) Villeneuve, M.; Kaneshina, S.; Imae, T.; Aratono, M. *Langmuir* **1999**, *15*, 2029.

(26) Meguro, K.; Ikeda, K.; Otsuji, A.; Taya, M.; Yasuda, M.; Esumi, K. *J. Colloid Interface Sci.* **1987**, *118*, 372.

(27) *The Tutorial of Instrument Analysis*; Division of Instrument Analysis of Chemistry Department, Peking University, Ed.; Peking University Press: Beijing, 1997; p 22.

(28) Mukerjee, P.; Cardinal, J.R. *J. Phys. Chem. B* **1978**, *82*, 1824.

(29) Soroja, G.; Samanta, A. *Chem. Phys. Lett.* **1995**, *246*, 506.

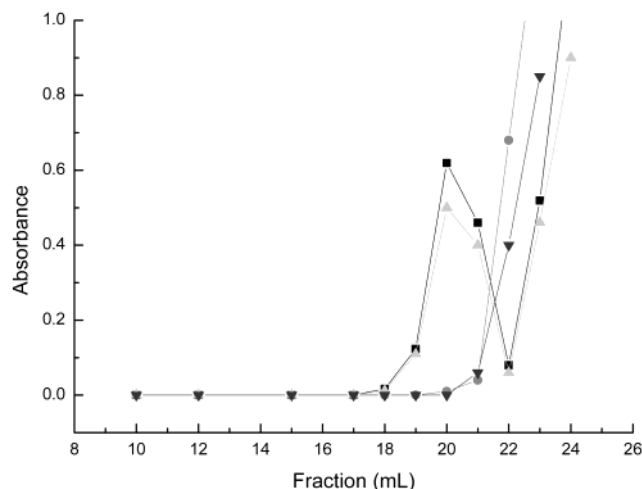


Figure 4. Encapsulation of bromophenol blue from $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS}$ mixtures for $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS} = 1:2$ [total surfactant concentration: (■) 1.0×10^{-3} mol/L; (●) 5.0×10^{-5} mol/L] and $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS} = 3:2$ [total surfactant concentration: (▲) 1.0×10^{-3} mol/L; (▼) 6.0×10^{-5} mol/L].

membrane. The similar result of blue shifts in the ethanol and in the $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS}$ mixture indicates that the microenvironment of the vesicle membrane is similar to that of ethanol. However, when the concentrations of mixed solutions were diluted to 5×10^{-5} mol/L, that is, the concentration at which elongated aggregates appeared, no apparent blue shift was observed, demonstrating that the surfactant molecules in the elongated aggregates were highly hydrated.

Encapsulation of aqueous compounds (drugs, perfumes, etc.) in their inner aqueous phase is one important characteristic of vesicles.³⁰ The dye encapsulation experiment was performed in $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS}$ systems at different concentrations (see Figure 4). The

samples were prepared in a 5×10^{-4} mol/L aqueous bromophenol blue solution and then aged at room temperature for 12 h to reach equilibrium. 0.4 mL samples were eluted with a 0.1 mol/L NaBr aqueous solution at a velocity of 0.5 mL/min on a $1.0 \text{ cm} \times 30 \text{ cm}$ column (Sephadex G-25 gel, medium grade). The excluded fractions were collected and checked on a Shimadzu UV-vis spectrophotometer at a wavelength of 590 nm to detect dye absorbance. The total amount of dye in each fraction was added up to get the encapsulation efficiency. Figure 4 represents the absorbance of bromophenol blue as a function of the elute volume. It can be seen from Figure 4 that, in both the 1:2 and 3:2 $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS}$ systems (1×10^{-3} mol/L), the absorbance of bromophenol blue begins to increase at the elute volume 18 mL, reaches the optimum at 20 mL, and then decreases. This indicated that bromophenol blue was entrapped into vesicles. The trapping efficiency was about 3%. After the elute volume was higher than 22 mL, the free dyes began to flow out and the absorbance sharply rose again. However, almost zero encapsulation was found in the 5×10^{-5} mol/L mixed systems, which indicated that the elongated aggregates did not have any trapping ability.

4. Conclusions

In summary, two breaks were observed in the surface tension curves of $(\text{N}^+-\text{C}_6-\text{BP}-\text{C}_6-\text{N}^+)/\text{SDS}$ systems. Vesicles and elongated aggregates existed respectively at the concentration in the range of the horizontal part and at that between the two breaks in the surface tension curves. Different from vesicles, the elongated aggregates could not solubilize or entrap dye molecules.

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Supporting Information Available: Synthesis of the bolaamphiphile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(30) Ravoo, B. J.; Darcy, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 4234.