Chalcogenide Letters Vol. 8, No. 6, June 2011, p. 391 – 395

EXPERIMENTAL AND SIMULATION OF LYOTROPIC MESOPHASE FORMATION OF SULFONATE GEMINI SURFACTANTS IN AQUEOUS SOLUTIONS

SEN ZHU[a*], LIJUAN LIU [a,b], FA CHENG[b]
[a]*Department of Materials Science and Engineering, Tianjin Institute of Urban Construction, Tianjin 300384 , People's Republic of China*
[b]*Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, People's Republic of China*

Four sulfonate Gemini surfactants with different spacer chain length were employed in this article. Their aggregation behaviors were investigated using transmission electron microscopy (TEM). Spherical micelles could be found from the images of TEM even below critical micelle concentration (cmc). With increasing of concentration, a transition from micelles to liquid crystals was detected of four surfactants and Gemini B has the lowest concentration to form new lyotropic phase. The lamellar phase was seen to form firstly by polarizing optical microscopy (POM). It is similar to the two-tail/one-head-group surfactants such as Phospholipid. And geometry optimization through energy minimization supports the result of TEM; ie., that the Gemini surfactant with odd spacer carbon numbers showing excellent efficiency at forming liquid crystal.

(Received May 26, 2011; Accepted June 21, 2011)

Keywords: Gemini surfactant, anionic surfactant, liquid crystal, geometry optimization.

1. Introduction

Dimeric or Gemini surfactants which are made up of two hydrophobic chains and two polar head groups covalently attached through a spacer at the level of the head groups or very close to these groups [1] are of current interest for their superior properties compared with those conventional ones.

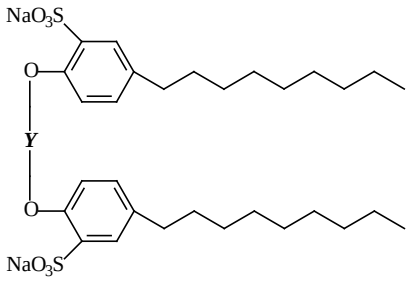
During recent years, many investigations have been reported on their unusual properties such as low critical micelle concentration (CMC), lower C_{20} (surfactant concentration in the solution phase that will reduce the surface tension of the solvent by 20 $mN.m^{-1}$) [1-4], better lime-soap dispersing properties [5], better wetting properties [6], low Krafft temperatures [7] and unusual rheological properties [8] *et al*. However, aggregation behavior of Gemini surfactants above cmc was seldom reported to our knowledge, which maybe an important aspect in their applications.

In our previous study, formation of a new phase of sulfonate Gemini surfactant in aqueous solution was observed. Here the mesomorphic behaviors of these surfactants were investigated by TEM and POM. Results showed that lamellar phase was seen to form first with increasing the concentration of surfactants and the surfactants with odd spacer chain number are more efficient in forming liquid crystals. And the results were interpreted from molecular level by optimized conformation of these surfactants through energy minimization.

* Corresponding author: zhusen@tjuci.edu.cn

2. Experimental

Four Gemini surfactants,
disodium mono(6,6'-(ethane-1,2-diylbis(oxy))bis(3-nonylbenzenesulfonate)) (Gemini A),
disodium mono(6,6'-(propane-1,3-diylbis(oxy))bis(3-nonylbenzenesulfonate)) (Gemini B), disodium mono(6,6'-(butane-1,4-diylbis(oxy))bis(3-nonylbenzenesulfonate)) (Gemini C), and disodium mono(6,6'-(hexane-1,6-diylbis(oxy))bis(3-nonylbenzenesulfonate)) (Gemini D),
were synthesized and purified according to the method described in our previous paper [2]. Their structures are shown in fig. 1. There is no minimum in the curves of surface tensions against concentrations.



Y	**abbreviation**
$-(CH_2)_2-$	Gemini A
$-(CH_2)_3-$	Gemini B
$-(CH_2)_4-$	Gemini C
$-(CH_2)_6-$	Gemini D

Fig. 1 chemical structure of Gemini surfactants

The images of the aggregates were determined on a transmission electron microscopy (TEM, JOEL JEM-2010) operated at 200 kV, and energy dispersive X-ray (EDX) analyzer (JEOL, JSM-6335F) operated at 15.0 kV. The textures of liquid crystals were recorded on a polarizing optical microscopy (XP-10, Guizhou optical instruments corporation). Geometry optimization process through energy minimization was performed using MM2 computations on chem3D software on a Pentium 4 3000 MHz processor computer with WindowsXP operating system.

3. Results and discussion

Fig.2 shows the images of TEM for the aggregates formed by Gemini C at different concentration. From the concentration below critical micelle concentration (cmc, 1.45×10^{-4}mol·L^{-1})[2], premicellar formation could be seen(Fig. 2a). With the increase of concentration to cmc value, spherical vesicles could be found (Fig. 2b). And the magnification image at the concentration of 7.55×10^{-4} mol·L^{-1}(5cmc) shows coexistence of spherical micelle and liquid crystals(Fig. 2c), which was demonstrated by the picture of electron diffraction(Fig. 2d) and agree with our previous work that the aggregation numbers of Gemini surfactants all go through a maximum for the formation of a new lyotropic mesophase[2].

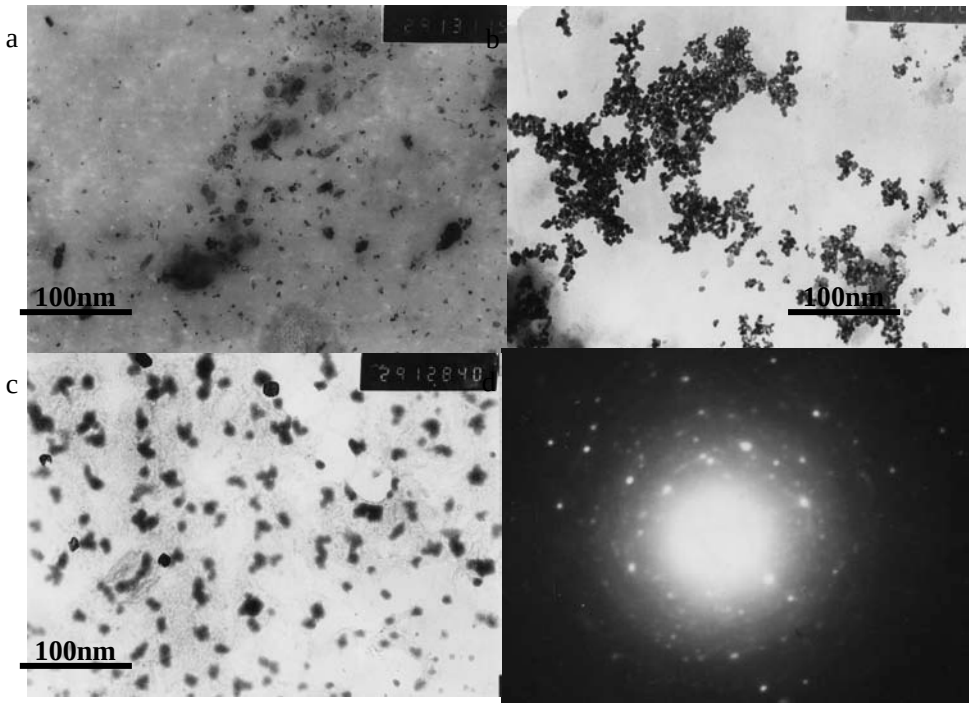


Fig. 2 TEM images of aggregates formed by Gemini C in aqueous solution. (a)c=3.80×10^{-5} mol·L^{-1};(b)c=1.45×10^{-4} mol·L^{-1};(c) c=7.55×10^{-4} mol·L^{-1}; (d)electron diffraction image at 7.55×10^{-4} mol·L^{-1}

The optical texture of the lyotropic mesophase was obtained by polarizing optical microscopy. At lower concentration, their typical pictures are shown in fig. 3. Cross-link textures can be observed form the picture, which demonstrated that it was a lamellar phase. This is opposite to the liquid crystal formation of conventional monomeric surfactants, but similar to the two-tail/one-head-group surfactants like Phospholipid. When dissolved in water, they form different phase in the following sequence (scheme 1).

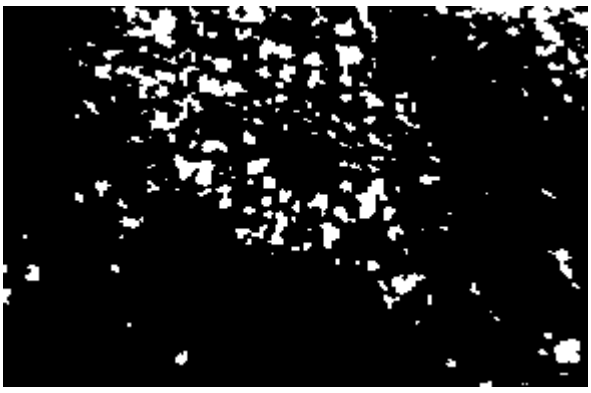


Fig. 3 Optical texture of Gemini surfactant in aqueous solution

$$\text{solid state} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{hexagonal phase} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{cubic phase} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{lamellar phase} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{micelle} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{isotropic solution}$$

Scheme 1 aggregate forming process with concentration of Gemini surfactants in aqueous solution

In our previous work, it was found that the aggregation numbers of these Gemini

surfactants all have an abrupt change for the formation of new phase and Gemini B has the lowest concentration to form liquid crystal. This maybe interpreted as follows. Lamellar liquid crystal formed by Gemini surfactants is a phase formed with double surfactant layers alternating with layers of water and the ionic head-groups lying at the interface between them. Its schematic diagram is shown in fig. 4. To form lamellar phase, two chains of the Gemini surfactant must be at the same side of the spacer and take on the shape as following.

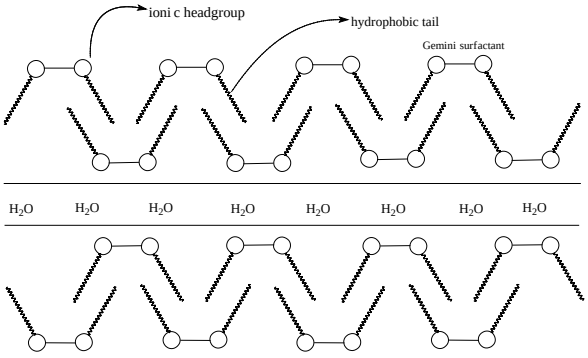
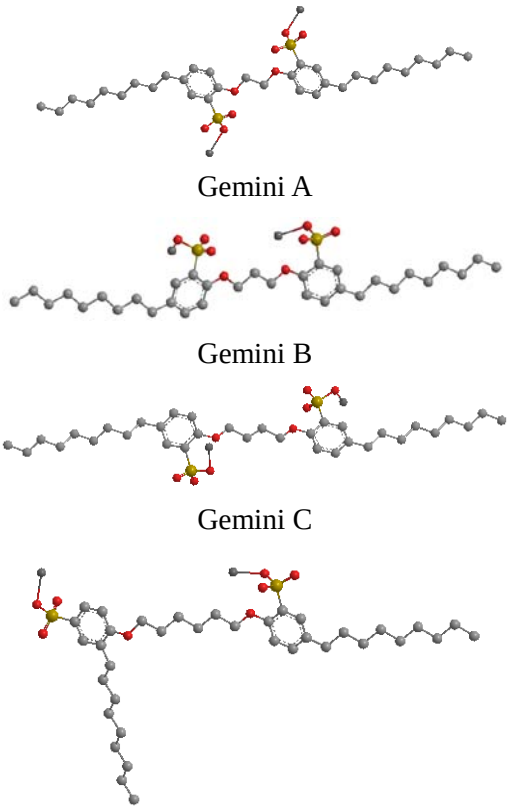


Fig. 4 Schematic diagram of lamellar phase formed by Gemini surfactant.

To understand the formation of the liquid crystal, Geometry optimization by energy minimization was operated to obtain their optimized structures. And this process is used to locate a stable conformation of a model before further analyses. **Fig. 5** presents the optimized conformation of four Gemini surfactants.



Gemini A

Gemini B

Gemini C

Gemini D

Gray-carbon; yellow-sulfur; red-oxygen; dark gray-sodium

Fig. 5 Optimized conformation of Gemini surfactants

From **fig. 5**, conclusion can be made that Gemini B can form lamellar phase without any transition of the structure while the rest surfactants must change their conformation to forming liquid crystals. This process causes the energy of the system raising and prevents the formation of the lamellar phase. So the conformational transition may account for the lowest concentration of Gemini B to form lamellar liquid crystal. Further research on the simulation of the aggregation behaviors for these Gemini surfactants will be investigated in our next paper.

4. Conclusion

Aggregation behavior of a series of sulfonate Gemini surfactants in aqueous solution was investigated in this paper. Phase transition from spherical vesicles to liquid crystal was seen from the TEM images for all four surfactants. And Gemini B, which has odd spacer chain number is more efficient in forming new phase. Form POM pictures lamellar phase was found at lower surfactant concentration. Geometry optimization through energy minimization was performed to further understand the unusual aggregates and optimized conformation of Gemini surfactants supports the result from TEM images.

References

[1] M. J. Rosen, Chem. Tech.**23**, 30 (1993)

[2] S. Zhu, F. Cheng, J. Wang, J.G. Yu, Colloids Surf. A **281**, 35(2006)

[3] X.L. Cao, Z.Q. Li, X.W. Song, X.H. Cui, Y.P. Wei, F. Cheng, J. Wang, J. Surfact. Deterg. **12**, 165(2009)

[4] J.P. Yang, J.Y. Xie, G.M. Chen, X.C.Chen, Langmuir **25**, 6100(2009)

[5] Y.P. Zhu, A. Masayama, M. Okahara, J. Am. Oil. Chem. Soc. **67**, 459(1990)

[6] Y.P. Zhu, A. Masayama, Y. Kobata, Y. Nakatsuji, M. Okahara, M.J. Rosen, J. Colloid Interface Sci. **158**, 40(1993)

[7] T.S. Kim, T. Kida, Y. Nakatsuji, T. Hirao, I. Ikeda, J. Am. Oil. Chem. Soc., **73**, 907 (1996)

[8] F. Kern, F. Lequeux, R. Zana, S.J. candau, Langmuir, **10**, 1714 (1994)