Study of Ordering for AOT/Water Lamellar Lyotropic Liquid Crystal: Small-angle X-ray Scattering Experiments[*]

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Abstract   Small-angle X-ray scattering (SAXS) is utilized to study the ordering of AOT/water lamellar phase. As increasing surfactant concentration, temperature or adding cosurfactant in certain range, the arrangement of hydrocarbon chains will change from sparse to dense which results in the structural transformation of lamellar phase from "flexible" to "planar" bilayers. The possible mechanism is proposed based on shape factor and molecular interactions. Molecular simulations are also carried out to testify the obtained results.

Keywords: SAXS,   Molecular simulation,   Lamellar phase

Lyotropic liquid crystal (LLC), depending on type of molecular assembling, is capable to reach special structure of aggregation by varying surfactant concentration and temperature[1-2]. Among them, lamellar phase is widely studied as a good template due to its stability and long-range periodic structure[3]. As a common anionic amphipathic molecule with two hydrophobic chains, sodium-1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) has been widely used in forming LLC. The AOT/water binary system has been studied for decades and confirmed to construct the lamellar phase in a broad AOT concentration range[4]. Prouzet *et al*.[5] studied water confined in lamellar structures of AOT using infra-red spectroscopy. Nuclear magnetic resonance experiments were done to discuss the influence of mechanical stresses on AOT/water system by Muzzalupo *et al*.[6]. The phase transition boundary of AOT surfactant solution was investigated using rheological techniques by Terentjev *et al*.[7]. The ternary systems of AOT are also extensively studied[8-9]. However, the detailed ordering of AOT/water binary system is little discussed in previous reports. Especially, there are different opinions about the mechanism of structural transformation[10-11].

The first observations of diffuse X-ray scattering at small angles, dating back to the early 1930s, were made on solid fibers and colloidal powders. Over the past decades, small-angle X-ray scattering (SAXS) has been developed as an useful tool for studying organized molecular assemblies[12-13]. Based on SAXS results, various phases with different Bragg peaks can be characterized and their long-range ordering is obtained, so that the interaction between molecules and the stabilization scheme of system can be explored[14-15]. In this paper, SAXS technique is utilized to characterize the lamellar structures constructed with changing AOT concentration, temperature or adding cosurfactant. The structural transition mechanisms, ordering of lamellar phase and interactions between molecules are discussed by analyzing SAXS curves based on shape factor and molecular interactions such as van der Waals force, electrostatic force, *etc*. Molecular simulations are also carried out correspondingly to exhibit definite lamellar phase.

1   Experimental

AOT (>98%) was purchased from Sigma. 1-octanol (A.R.) as cosurfactant was obtained from Hengye Jingxi Chemical Co. LTD and the water used in the experiments was double distilled. The binary system AOT/water and the ternary system AOT/1-octanol/water were prepared in glass tubes. The samples were shaken up and centrifuged with 4000 r·min^{-1} for three times, then sealed for 15 days at 20 ℃ before further study. The mass fraction of 1-octanol was 0.03 for all ternary systems.

Small-angle X-ray scattering experiments were operated at

298 K by means of a Kratky compact small-angle system equipped with a position sensitive detector(OED 50 M from Mbraun, Graz, Austria) containing 1024 channels of width 54 mm. The range of scattering angle was chosen from h=0.05 to 6 nm^{-1}, where the magnitude of scattering vector h=2πsinθ / λ, 2θ and λ being, respectively, the scattering angle and incident X-ray wavelength of 0.1542 nm. The distance from sample to de-tector was 27.7 cm and the exposure time was 600 s for each sample.

2   Results and discussion

2.1   LLC lamellar structure with varieties of surfactant concentration

Fig.1 shows the scattering curves of AOT/water system as a function of mass fraction φ of AOT. There is only one peak at low φ shown in Fig.1(a), which cannot be defined as lamellar phase. Two scattering peaks can be distinguished and become sharper with increasing surfactant concentration, which show the appearance of lamellar phase and enhanced ordering. According to shape factor, $v/a_0 l_c$, where v is hydrocarbon volume, a_0 is the optimal surface area per molecule and l_c is critical chain length, it can be determined that AOT molecules might form micelles ($v/a_0 l_c < 0.5$) or bilayers   ($0.5 < v/a_0 l_c < 1$)[16]. The quantity of AOT is small at low φ and headgroups contact well with water. This leads to larger a_0 and makes the system tend to form micelles. With surfactant concentration increasing, the hydrophobic attraction will be improved, which may induce molecules to associate and decrease a_0 so that bilayers occur. Fig.1(d) and 1(e) give the scattering curves at φ=0.4 and 0.5, respectively. The peaks for φ=0.5 are sharper than those for φ=0.4. Therefore the ordering of the former is better than the latter. This is because the structure of lamellar phase depends not only on the shape factor but also on many interactions, such as van der Waals, electrostatic, hydration and steric forces[16]. These interactions cannot operate in a long distance. For example, van der Waals forces decay with D^2 (where D is the distance between bilayers). The lower thickness of water layer is beneficial for van der Waals attraction.
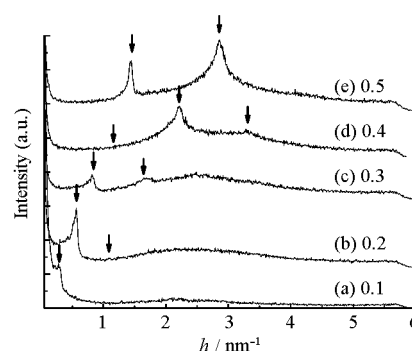

Fig.1   Scattering curves of the AOT/water system with φ=0.1, 0.2, 0.3, 0.4 and 0.5

The range of hydration forces so far measured between various surfactant bilayers is usually less than 3 nm. As shown in Fig.1, the thicknesses of water calculated using a formula suggested by Kotlarchyk[17] between bilayers are about 2.1 and 3.4 nm for φ= 0.5 and 0.4 respectively. Meanwhile the quantity of ions will increase with AOT concentration that is favorable for the stability of electrostatic double layer.

Recently, computer simulation has become a powerful tool for the study of surfactant systems. The dissipative particle dynamics (DPD) method introduced by Hoogerbrugge and Koelman in 1992[18] is an effective mesoscopic dynamics technique, bridging the gap between atomistic and macroscopic simulation. This technique allows the simulation of hydrodynamic behavior in much larger systems that contain millions of atoms up to microsecond range[18-23]. The parameters used for carrying out DPD simulation can be obtained from Flory-Huggins-type theory[21]. Fig.2 shows model structures of AOT/water lamellar phase from molecular simulation using Cerius^{II}. There are only some spherical and plate-like micelles when φ=0.1 corresponding to Fig.1 (a). As surfactant concentration increases, bilayers appear and the ordering of lamellar phase becomes better, which agree well with SAXS experimental results. However, there is a range around φ=0.4 where AOT molecules cannot form well-defined lamellar phase. As shown in Fig.2(d), there are some defective structures at φ=0.4 with micelles or surfactant "bridges" between
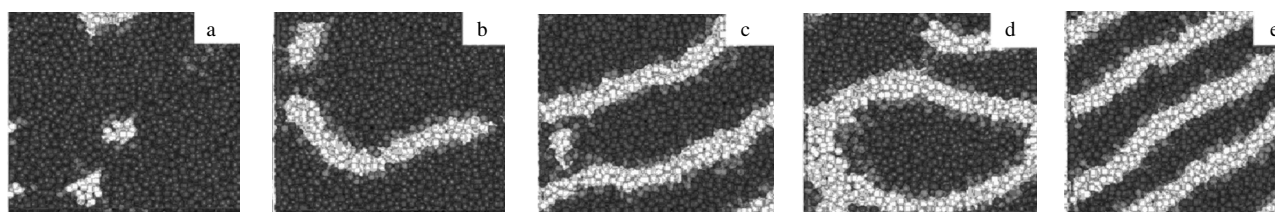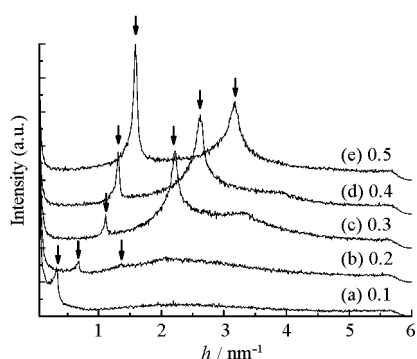

Fig.2   Molecular simulated phase structures of the AOT/water system with φ=0.1, 0.2, 0.3, 0.4 and 0.5 for a, b, c, d, and e, respectively
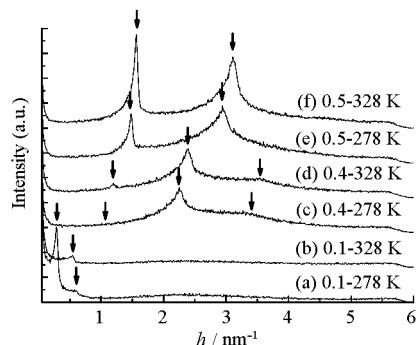
Fig.3 Scattering curves of the AOT/water/1-octanol system with φ=0.1, 0.2, 0.3, 0.4 and 0.5

bilayers. Such deformed lamellar structures result in only a very weak first peak to be observed from SAXS curve (see Fig.1(d)) due to much sensitivity of SAXS to small structural fluctuations of lamellae[24], especially to "neighboring" bilayers. Fontell[11] also reported this phenomenon but he didn't explain the possible reason. This will be discussed later.

2.2 Cosurfactant effect on LLC lamellar structure

Fig.3 illustrates the effect of cosurfactant on AOT organized assemblies. There are two peaks observed obviously at φ= 0.2 when adding a little 1-octanol to form the ternary system as shown in Fig.3(b), which is similar to Fig.1(c) where φ=0.3 and no cosurfactant adding. The first scattering peak also occurs with φ=0.4 (compared to Fig.1(d)) and becomes sharper when φ=0.5 than no cosurfactant (see Fig.1(e)). The long-range ordering of lamellar phase is improved evidently by analyzing the scattering peaks with Scherrer equation[3]. This is because the effective hydrocarbon volume, v, is increased due to the penetration of organic molecule, such as low MW alkanol, into the chain regions. It results in the increased value of $v/a_0 l_c$ and bilayer appearance at low φ, as well as the high ordering of lamellar phase at high φ.

2.3 LLC lamellar structure at different temperatures

**Fig.4 Scattering curves of the AOT/water system at different temperatures**

Table 1 Repeat distances (d) of AOT/water and AOT/water/1-octanol lamellar phases

φ	d / nm			
	AOT/water			AOT/water/1-octanol
	T=278 K	T=293 K	T=328 K	T=293 K
0.1	20.8	Non-lamellar	Non-lamellar	Non-lamellar
0.2	10.8	10.6	10.0	9.1
0.3	7.5	7.3	7.1	5.6
0.4	5.6	5.4	5.3	4.8
0.5	4.2	4.1	4.0	3.9

d is the periodic distance of lamellae determined by AOT bilayer (with or without cosurfactant) and water layer.

Both a_0 and l_c can be changed with temperature. Such effects are subtle and generally less well understood because a_0 usually increases due to the enhanced steric repulsion between headgroups and l_c decreases because of the hydrocarbon chain motion involving trans-gauche isomerization as increasing T. Then shape factor $v/a_0 l_c$ may decrease or increase with temperature. As shown in Fig.4, lamellaes occur at φ=0.1 and T=278 K but vanish when increasing T. It implies that both molecules motion and a_0 will be weakened with decreasing T, which is favorable for larger aggregate such as AOT bilayers. However, the first scattering peak occurs at φ=0.4 and sharpens at φ=0.5 when T increases from 278 to 328 K. It shows that the ordering of lamellar phase will be improved. This is because l_c is reduced by 0.3 and 0.2 nm respectively, assuming the thickness of water is constant for the same φ at different temperatures. In addition, the curvature modulus of surfactant bilayers may be increased with temperature and the AOT headgroup conformation will change due to dehydration, which will enhance the lamellar phase order[25]. All repeated distances measured at different conditions are summarized in Table 1.

Combined with the effects of AOT concentration and cosurfactant, we think that the surfactant molecules may undergo a reorganization when φ=0.4, where the arrangement of hydrocarbon chains will change from sparse to dense status and meanwhile the structure of lamellar phase will transform from "flexible bilayer" to "planar bilayer" as shown in Fig.5.

flexible bilayer   planar bilayer
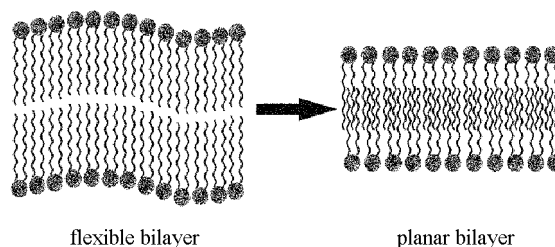
Fig.5 Schematic description on structural transformation of lamellar phase

3 Conclusions

Here we analyze SAXS curves of lamellar phases and discuss the mechanism of structure transformation based on shape factor and various molecular interaction. Increasing surfactant concentration, temperature and adding cosurfactant in certain range, lamellar phase will change from "flexible bilayers" to "planar bilayers" and the high ordering of LLC will be obtained.

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小角 X 射线散射表征 AOT/水层状溶致液晶的有序性 [*]

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摘要   用小角 X 射线散射研究了 AOT/水层状溶致液晶的有序性. 通过对散射曲线的解析, 讨论了表面活性剂浓度、温度和助表面活性剂等三个方面对溶致液晶层状相结构有序性的影响. 在一定的范围内, 提高温度, 改变表面活性剂浓度和加入少量助表面活性剂可使碳氢链排列由稀疏转变为密实, 层状相也相应地由"柔性双层"过渡到更加有序化的"平面双层". 基于形状因子和体系内分子间作用力, 提出了层状相形成与有序化的机理, 同时采用分子模拟的方法展现了不同浓度下的液晶结构.

关键词：   小角 X 射线散射, 分子模拟, 层状相
中图分类号：   O648