Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Wärnheim, TorbjÖRn , Henriksson, Ulf , Malmvik, Ann-Charlotte and Bergenståhl, Björn(1988) 'Alkyl chain order in a lamellar lyotropic liquid crystal with varying surface charge density', Liquid Crystals, 3: 6, 791 — 795
To link to this Article: DOI: 10.1080/02678298808086535
URL: http://dx.doi.org/10.1080/02678298808086535

LIQUID CRYSTALS, 1988, VOL. 3, NOS. 6 AND 7, 791–795

Alkyl chain order in a lamellar lyotropic liquid crystal with varying surface charge density

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The alkyl chain order in the lamellar liquid-crystalline phase formed in the octylamine/octylammonium chloride/water system has been investigated by ^2H N.M.R. at constant mole ratio water/amphiphile and varying charge of the lamellae. The results are correlated to the dimensions of the aggregate obtained from X-ray low angle diffraction measurements.

1. Introduction

Amphiphiles form a variety of lyotropic mesomorphic phases including hexagonal, lamellar and cubic phases [1, 2]. While many of the details regarding their structure have been elucidated, several questions are only partially answered. Some fundamental questions are concerned with the ordering of the alkyl chain within the aggregate. How is the alkyl chain order affected by the phase structure and the aggregate dimensions; or vice versa, how does the conformational state of the surfactant affect the stability of aggregates of different shape [3, 4]? In view of the relatively few systems which have been systematically investigated, it is relevant to look for suitable model systems. In our investigations [5, 6] we have chosen the octylamine/octylammonium chloride/water system [7], which forms a lamellar lyotropic liquid-crystalline phase over a wide composition range (figure 1). In this phase the surface charge density can be varied from roughly $\lesssim 1$ charge/5000 Å^2 in the octylamine/water lamellar phase (assuming a pKa ~ 10 for octylamine [8]) to 1 charge/35 Å^2 in the octylammonium chloride/water lamellar phase.

The aggregate dimensions were determined from X-ray low angle diffraction and the conformational state of the surfactant alkyl chain was monitored by ^2H N.M.R. Measurements have been performed at a constant mole ratio water/amphiphile = 4/1 along the dashed line in figure 1 [5]. The effects on the order parameters when adding *p*-xylene as a solubilizate or changing the temperature were also studied. In addition, these directly measured order parameters are compared with equivalent order parameters obtained from analysis of the frequency dependence of the ^2H nuclear magnetic relaxation of deuterium labelled surfactant [6].

2. Experimental

Chemicals: octylamine (Fluka 99 per cent), octylammonium chloride (Eastman-Kodak) and *p*-xylene (Aldrich, 99 per cent +) were used without further purification. α-deuterated octylamine was prepared from caprylonitrile, and per-deuterated

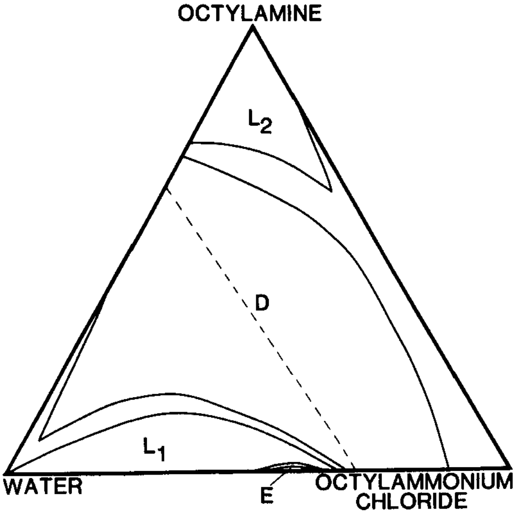

Figure 1. The phase diagram of the ternary system octylamine/octylammonium chloride/water at 20°C. L denotes isotropic solution phases, D denotes a lamellar phase, E denotes a hexagonal phase; the unmarked regions include two-phase regions and three-phase triangles. From [7]. The experiments were performed along the dashed line corresponding to a constant mole ratio water/(octylamine + octylammonium chloride) = 4/1.

octylamine from the commerically available octanoic acid [5]. Water was twice distilled.

N.M.R. measurements of quadrupolar splittings were performed on a Bruker CXP-100 spectrometer operating at 13·82 MHz for ^{2}H at 20°C. Repeated distances were determined with an X-ray low angle diffraction camera equipped with a position sensitive detector (PSD-100, Tennelec). The dimensions of the bilayer were calculated from the repeat distance using the following specific volumes of the components: 1·00 ml/g for water [9], 1·28 ml/g for octylamine [9] and 1·10 ml/g for octylammonium chloride [10].

3. Results and discussion

In the binary octylammonium chloride/water system the area per polar group is high, around 34 Å^2 at a mole ratio 1/4 (figure 2). Decreasing the charge density of the lamellae by replacing octylammonium chloride with amine leads to decreasing lateral repulsion in the head group region and a subsequent change in area. Qualitatively these results are similar to those obtained for three-component systems water/alcohol/surfactant [2]. The similarity between the role of the alcohol and the role of the amine is very obvious also from a comparison between the phase diagram in figure 1 and one where octylamine has been replaced by decanol [2]. The phase diagrams are very similar up to a mole ratio uncharged/charged amphiphile ~ 1/1. At higher mole ratios of uncharged component, the differences in solution behaviour between alcohol and amine become important. In the alcohol containing systems, the lamellar phase becomes unstable and a miscibility gap between the alcohol and the water appears [2].

The area per polar group does not change very much when the fraction of uncharged surfactant exceeds 0·5. The area here is around 28 Å^2 which is slightly above the minimum values obtained in lamellar phases, around 25–26 Å^2 per polar group [2].

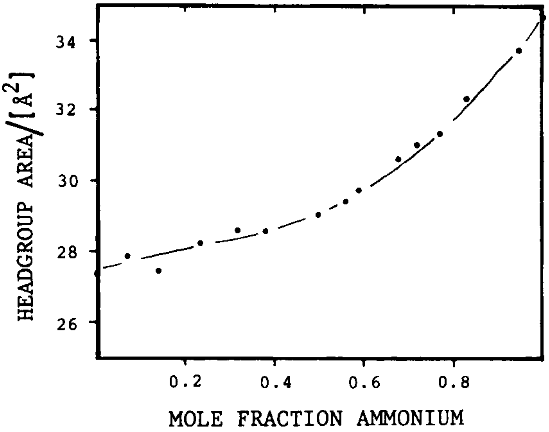

Figure 2. Area per polar group at 20°C for samples along the dashed line in figure 1.

It is likely that steric constraints in the alkyl chain region become important for determining the bilayer dimensions at these compositions.

The conformational states of the surfactant alkyl chain have been monitored by means of quadrupolar splittings in the ^{2}H N.M.R. spectra. For a polycrystalline sample, the splitting δ is related to the order parameter S according to

$$\delta = 3/4\, \chi S, \tag{1}$$

where χ is the coupling constant, set to 167 kHz, and the order parameter S is given by the time average

$$S = 1/2\, \langle 3\cos^2\theta - 1 \rangle, \tag{2}$$

where θ is the time dependent angle between the C–D bond and the director perpendicular to the lamellae.

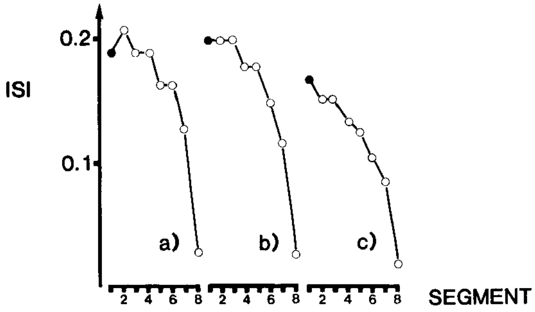

Figure 3. Order parameter profiles along the surfactant alkyl chain for samples along the dashed line in figure 1. (●) is from α-deuterated and (○) from per-deuterated surfactant. Mole ratios amine/ammonium chloride: (*a*) 1/0; (*b*) 1/1; (*c*) 0/1.

Some order parameter profiles for different samples are shown in figure 3. Only one average order parameter for the amine and the ammonium chloride are observed due to the rapid proton exchange between amine and ammonium groups. The order parameter for the α-segment is unambiguously assigned using selectively deuterated amine. For the other segments a decreasing order parameter along the chain has been assumed [11].

In figure 4, the order parameters are plotted versus the area per polar group as determined by X-ray diffraction. In the highly charged systems at high areas all

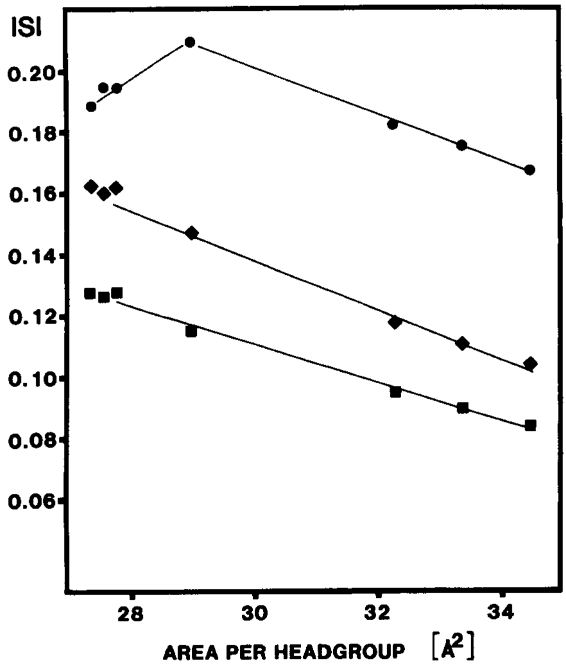

Figure 4. Order parameter for different methylene segments in the surfactant alkyl chain versus the area per polar group. ●, α-methylene segment; ◆, (ω-2)-methylene segment; ■, (ω-1)-methylene segment.

segments along the chain follow a linear relation, similar to what has been found in other systems [12]. Thus, the constraints imposed by the aggregate dimensions seem to dominate the ordering in large parts of the lamellar phase. However, in the amine-rich region, the segments closest to the polar group have a decreasing order parameter in spite of a slightly decreasing area (figures 3 and 4). Two explanations are evidently viable:

at low charge densities the area is mainly determined by the interactions in the alkyl chain region and at the lowest charge densities the amplitude of the reorientational motions for the segments closest to the polar interface might increase;

a change in orientation of the polar group and the first methylene segment of the alkyl chain occurs at the lowest charge densities.

Another rather interesting difference between octylamine and octylammonium chloride becomes obvious when comparing the two binary systems with water. The octylamine/water system forms a lamellar phase which is very sensitive to a temperature increase (melting point maximum at 35°C) [13] and to addition of solubilizate, for example *p*-xylene (maximum 6 wt % *p*-xylene at 20°C and 3 wt % at 27°C) [14]. This can be compared to the octylammonium chloride/water system with a melting point for the lamellar phase > 100°C and a solubilizing capacity for *p*-xylene corresponding to 20 wt % at 20°C [2]. These differences are illustrated by the order parameters presented in the table: while an increase in temperature or solubilization of *p*-xylene considerably lowers the order parameters in the octylamine/water lamellar phase, there is no effect or a small increase, respectively, in the octylammonium chloride/water system.

Order parameters for the α-methylene segment in some different systems.

System	Directly measured in the lamellar phase 20°	27°	Obtained from analysis of relaxation data 27°
Octylamine/water	0·180 (*a*)	0·156 (*a*)	0·157 (*b*)
Octylamine/water/xylene		0·133 (*c*)	0·122 (*d*)
Octylammonium chloride/water	0·167 (*e*)	0·168 (*e*)	
Octylammonium chloride/water/xylene		0·175 (*f*)	

Compositions (weight ratios): (*a*) 50 : 50; (*b*) 20 : 80; (*c*) 48 : 49 : 3; (*d*) 48 : 48 : 4; (*e*) 70 : 30; (*f*) 63 : 27 : 10.

The directly measured order parameters in the lamellar phase can be compared with the equivalent order parameters derived from the frequency dependence of the ^2H relaxation rates of deuterium labelled surfactant in isotropic solution phases. The relaxation rate in isotropic phases can be interpreted according to a two-step model with motions occurring on different timescales [15, 16]. The rapid local anisotropic motions averages the quadrupole interaction to χS where the order parameter S is defined as in equation [2], but the time average should be taken over times which are long compared to the local motion but shorter than the timescale of the aggregate motions. The numerical values of S obtained from analysis of relaxation data for some samples in the solution phase [6] are also shown in the table. The similarities with the order parameters directly measured in the lamellar phase are consistent with the notion that the local state of the surfactant, as reflected by the order parameter of the α-methylene segment, is very similar in the lamellar liquid crystal and in the aggregates that exist in the isotropic solution phase close to the phase boundary.

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