Counterion and composition effects on discotic nematic lyotropic liquid crystals  
I. Size and order

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Abstract

Counterion and composition effects on the size and interface dynamics of discotic nematic lyotropic liquid crystals made of tetradecyltrimethylammonium halide (TTAX)–decanol (DeOH)–water–NaX, with X = Cl− and Br−, were investigated using NMR and fluorescence spectroscopies. The dynamics of the interface was examined by measuring deuterium quadrupole splittings from HDO (0.1% D2O in H2O) and 1,1-dideuterodecanol (20% 1,1-dideuterodecanol in DeOH) in 27 samples of each liquid crystal. Aggregation numbers, ND, from 15 samples of each mesophase were obtained using the fluorescence of pyrene quenched by hexadecylpyridinium chloride. ND of TTAB and TTAC are about 230 ± 30 and 300 ± 20, respectively. ND of TTAC increases with increasing concentration of all mesophase components, whereas TTAB shows no correlation between size and composition. The dimension of these aggregates prevents the occurrence of undulations, previously observed in lamellar phases. The quadrupole splitting of decanol-d2 in TTAC is about 5 kHz smaller than in TTAB, and the splitting of HDO is observed only in TTAB. All results are consistent with a more dynamic TTAC interface. The TTAC aggregate should be more dissociated from counterions and the excess ammonium–ammonium electrostatic repulsions contribute to increase the mobility of the interface components.

Keywords: Interface dynamics; Aggregation number and composition; Discotic nematic lyotropic liquid crystal

1. Introduction

Amphiphiles dissolved in water at a certain concentration and ionic strength form aggregates of different shape and size [1,2]. It is possible to obtain a wide variety of structures such as spherical and cylindrical micelles, vesicles, lamellar and hexagonal smectic phases, discotic and calamitic nematic mesophases, and others. All these aggregates have in common the existence of at least three different regions: (a) the aqueous region, which contains dissolved counterions, added salt and a small amount of free amphiphiles, (b) the interface, composed of headgroups, ions and water, and (c) the hydrophobic core made of linear aliphatic chains. Perhaps the most interesting region is the interface, since most electrostatic interactions take place there. Forces among charged and polar headgroups of the amphiphiles with ions and solvent molecules, at the interface, play a significant role in the determination of the size and shape of the aggregates [3,4]. In particular, discotic nematic lyotropic liquid crystals (type II [5]) are four-component mesophases made of oblate shaped bilayer aggregates, which form spontaneously in concentrated aqueous solutions of a charged amphiphile, decanol and salt. These aggregates spontaneously orient in the NMR magnetic field with the symmetry axis of the disk perpendicular to the direction of the field [6,7]. A static fluorescence quenching and molecular dynamics study about the size and structure of a discotic nematic aggregate made of tetradecyltrimethylammonium...
chloride (TTAC)/decanol (DeOH)/sodium chloride/water, concluded that the flat micelle is made of 258 amphiphile units (TTAC + DeOH), with an approximate radius of 3.8 nm [8]. It is well known that aggregation numbers measured using the static fluorescence quenching method, \(N_S\), are underestimated; the dynamic fluorescence quenching method gives better results [9]. To re-examine the size of the aggregate in TTAC and a previously reported four components SDS mesophases [10], and to study counterion and composition effects on the size and interface dynamics of nematic discotic lyotropic liquid crystals, we have carried out a comparative study between two mesophases prepared with TTAX–DeOH–H\(_2\)O–NaX, where X = Cl\(^-\) and Br\(^-\). The concentrations of all components, except water, were modified. The size of the aggregates were measured using dynamic fluorescence quenching of pyrene by hexadecylpyridinium chloride (HDPC) [11,12]. On the other hand, the dynamics of the interface was probed by measuring \(^2\)H NMR quadrupole splittings from 1,1-dideuterodecanol and monodeuterated water. \(^35\)Cl NMR quadrupole splittings were measured for the TTAC mesophase.

2. Materials and methods


### 2.1. NMR samples and spectra

TTAB and HDPC were purchased from Aldrich and TTAC from Anatrace. They were recrystallized three times from ethyl acetate/ethanol solutions before use. SDS was prepared and purified using a previously reported methodology [13]. Anhydrous NaCl, NaBr and Na\(_2\)SO\(_4\) were purchased from Aldrich and used without further purification. Decanol from Aldrich and used without further purification. Decanol was purified by fractional crystallization and enriched with 20% v/v 1,1-dideuterodecanol, previously synthesized by reduction of decanoic acid with LiAlD\(_4\) and purified by vacuum distillation. The compositions of all samples are listed in Tables 1 and 2. The samples were allowed to equilibrate at least 72 h at 300 K before measurements. \(^2\)H NMR spectra were obtained at 300 K in a Bruker Avance 400 spectrometer, using a BB inverse probe tuned to the \(^2\)H frequency (64.1 MHz). A 90° pulse length of 19 μs and a spectral window of 25 kHz were used in all \(^2\)H NMR spectra. \(^35\)Cl NMR spectra were recorded at 71.7 MHz, using the same spectrometer with the same probe and temperature. A 90° pulse length of 20 μs and a spectral window of 35 kHz were used. More than 4000 transients were accumulated and stored in 32 kB files.

#### 2.2. Time-resolved fluorescence quenching

Pyrene 99% was purchased from Aldrich and used as received. To investigate the size of the aggregates, experiments measuring the dynamic fluorescence quenching of added pyrene by added HDPC, according to a previously reported method developed for spherical micelles [14-17], were carried out in 15 samples of each mesophase. We briefly describe now the employed methodology. If both the fluorescent probe (pyrene) and the quencher (HDPC) are 100% associated to the micelle, and the distribution of quenchers into the aggregates follows the Poisson distribution, the time-resolved fluorescence decay data can be explained in terms of the following equation:

\[
I(t) = I(0) \exp\left(-kqt - B\left(1 - \exp(-kqt)\right)\right),
\]

where \(I(0)\) and \(I(t)\) denote the fluorescence intensities of pyrene at times zero and \(t\), following the excitation, and \(B = [Q]/[\text{Micelles}]\) is the average number of quenchers per micelle, the so-called occupation number. \(k_0\) is the decay rate constant of the probe in the absence of quencher, and \(k_q\) is the quenching rate constant. Therefore, the value of the micelle aggregation number \(N_D\) is obtained from the equation:

\[
N_D = B\frac{[S] - \text{cmc}}{[\text{HDPC}]},
\]

where [S] is the total molar concentration of surfactant molecules, [TTAX] + [DeOH]; cmc is the concentration of free amphiphiles, negligible compared to [S], and [HDPC] is the concentration of quencher. The aggregation number is obtained from the slope of a plot of \(B\) vs [HDPC], multiplied by [S].

We used the described methodology to measure the aggregation number of these TTAX and SDS disk shaped micelles. For this purpose, 5 μl of a stock solution of pyrene, \(4 \times 10^{-3}\) M in acetonitrile, were placed in a 25 ml flask and after evaporation of the solvent 5 ml of the corresponding mesophase were

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of mesophases(^a)</th>
<th>Quadrupole splittings(^b)</th>
<th>(N_D)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTAC</td>
<td>NaCl Decanol H(_2)O Decanol-d(_2)</td>
<td>(^{35})Cl</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.611 0.931 0.231 27.8 12448 9125 280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.611 0.931 0.241 27.8 14079 11525 316</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.611 1.034 0.231 27.8 14145 10693 314</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.611 1.034 0.241 27.8 15192 11398 351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.638 0.931 0.241 27.8 12578 10452 338</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.638 1.034 0.231 27.8 12339 9370 335</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note. The splitting of HDO was not observed in any sample of this mesophase. The estimated error in the quadrupole splittings are ±30 Hz for decanol and chloride, and the estimated error in the determination of \(N_D\) is ±20.

\(^a\) Values in mmol.

\(^b\) Values in Hz.

\(^c\) \(N_D\) is the aggregation number.
added. The solution was allowed to equilibrate at 300 K for 72 h and divided into 6 samples. Small amounts of a 0.2 M stock solution of HDPC were added to each sample, covering a concentration range from $9.1 \times 10^{-4}$ to $8.2 \times 10^{-3}$ M, and were allowed to equilibrate for another 72 h at 300 K before measurements. Time-resolved fluorescence decay curves were obtained at 300 K by exciting the samples with a LSI nitrogen laser, which provides 4 ns pulses at 337.1 nm, and detecting with an IP-28 photomultiplier (Hamamatsu) the emission passing through an Oriel 77250 monochromator. The decay was recorded in a digital Tektronik TDS 430A oscilloscope. Steady state fluorescence spectra were recorded with a SLM-Aminco SPF-500C spectrofluorimeter.

3. Results

To corroborate that the different solutions correspond to the same discotic nematic phase, polarized light microscopy textures were obtained using a MOTIC B3 microscope. Photographs of selected magnetic field oriented samples, obtained in the direction of the field, are shown in Fig. 1 [18]. Figs. 2 and 3 are the $^2$H NMR spectra of TTAC and TTAB from samples 14 and 49, respectively. The external doublet is assigned to the quadrupole splitting of decanol and the internal signal is assigned to HDO. $^{35}$Cl NMR spectrum from sample 14 appears in Fig. 4. All splittings were measured directly from the spectra. Tables 1 and 2 list the $^2$H quadrupole splittings of HDO and 1,1-dideuterodecanol from selected samples of TTAC and TTAB, as well as the quadrupole splittings of $^{35}$Cl from the TTAC mesophase. Fig. 5 shows a typical time-resolved fluorescence decay curve from pyrene and the best fit to function (1) to obtain the value of $B$. Fig. 6 shows a typical plot of $B$ vs the concentration of HDPC. In this case, the figure corresponds to sample 1. Tables 1 and 2 also list the values of $N_D$ measured in 15 samples of each mesophase. The complete version of Tables 1 and 2 are provided as supporting material. The aggregate size of a sodium decyl sulfate mesophase (SDS/DeOH/Na$_2$SO$_4$/H$_2$O) was previously estimated using small angle diffraction X-ray scattering.

![Fig. 1. Polarized light microscope textures of samples 1 and 27 of the TTAC mesophase (A and B) and samples 28 and 54 of the TTAB mesophase (C and D). The photographs were obtained along the direction of the applied magnetic field.](image)

![Fig. 2. $^2$H NMR spectrum from sample 14 of the TTAC mesophase. The quadrupole splitting of HDO was not observed in any TTAC sample. The insert is an expansion of the signal from HDO.](image)
Fig. 3. $^2$H NMR spectrum from sample 49 of the TTAB mesophase. The quadrupole splitting of HDO can be measured from the spectrum, as seen in the insert.

Fig. 4. $^{35}$Cl NMR spectrum from sample 14 of the TTAC mesophase. The quadrupole splittings can be measured directly for the spectra.

Data (SAXS) [10]. We have measured $N_D$ in the same sample using the dynamic fluorescence quenching method and the value is $236 \pm 25$.

4. Discussion

The textures observed in Fig. 1 allow concluding that all samples correspond to the same mesophase. As observed from Figs. 2 and 3, the quadrupole splitting of HDO is resolved only for the TTAB mesophase; only one peak arises from HDO in all TTAC sample spectra. A comparison between the deuterium quadrupole splittings of 1,1-dideuterodecanol from TTAB and TTAC mesophases, in equimolar samples (see Tables 1 and 2), reveals that the splittings measured in TTAB are about 5 kHz bigger than the splittings measured in TTAC. Carbon 1 (C$_1$) of decanol is very likely to be located in the internal region of the interface. The quadrupole splitting from the deuterium atoms attached to C$_1$ indicates the degree of alignment of the head group of decanol with the magnetic field, and reflects the dynamics of the interface. Circumstances that influence the degree of order of the micelle, such as the size of the aggregate or the internal dynamics, are expected to influence this splitting. The observed differences may have at least two origins: (1) the interface of the TTAB aggregate accommodates more oriented water molecules exchanging with isotropic solvent, either because it is thicker or the aggregate is bigger, or (2) the TTAC interface is more mobile than the TTAB interface, allowing decanol and the associated water molecules to move more freely.

An inspection of Tables 1 and 2 reveals that $N_D$ of the TTAB aggregate is always smaller than $N_D$ of TTAC. Another piece of evidence to support this result comes from viscosity measurements. The viscosity of the TTAC mesophase, measured with an Ostwald viscometer, is 2.1 times greater than the viscosity of the equimolar TTAB mesophase, consistent with a bigger TTAC aggregate. The aggregation number of sample 14 was measured in a previous work [8] employing a method based on the static fluorescence quenching of pyrene by HDPC, and the result was $N_D = 258 \pm 25$. Using the time-resolved fluorescence determination of $N_D$ gives a bigger value [9,19].

SAXS data, collected from a magnetic field oriented mesophase made of sodium decyl sulfate (SDS)/decanol/sodium sulfate/water, are consistent with an oblate shaped bilayer of am-
phiphiles. From the absence of diffractions perpendicular to the bilayer plane, the radius of the oblate was estimated to be approximately 25 nm [10]. Since this nematic mesophases preserve only orientational order along the direction of the field, i.e. only the symmetry axis of the oblate orients perpendicular to the direction of the magnetic field and there is no other restriction to the motion, an alternative interpretation of this result can be provided. The aggregate could be smaller with high mobility along the direction of the field. In the absence of order there is not repeating distance and no scattering should be observed. Our estimation of $N_D$ for the reported four components SDS mesophase [10] is equal to $236 \pm 25$, significantly smaller than expected from a 25 nm radius oblate. At least two determinations of the diameter/thickness ratio ($\rho$) of the oblate in anionic mesophases have been published in the past. Using X-ray and neutron scattering, Hendrikx and co-workers examined a three-component mesophase, made of SDS/DeOH/D$_2$O, and found a value of $\rho < 3$ [20]. Few years later using $^2$H and $^{23}$Na NMR relaxation, Furó and co-workers determined $\rho$ for a similar SDS/DeOH/H$_2$O mesophase and reported a value of $\rho$ between 3 and 4 [21]. The measured values of $N_D$ for the different mesophases studied in this work allow an estimation of the radius of the oblate shaped micelle in the range from 3.5 to 4.2 nm. Taking the value of $\rho = 3.0$ nm [20,21], and using 3.0 nm for the thickness of the bilayer gives a radius of 4.5 nm for the oblate, in agreement with the results obtained in the present work.

The data in Table 1 show that an increment of about 4% in the concentration of decanol induces an increase of approximately 30 units in $N_D$ of TTAC. The size of the micelle also increases with increasing ionic strength; in effect, $N_D$ increases in 35 units with a 12% increase in the concentration of salt, possibly due to a more effective shielding of the repulsive electrostatic interactions among the ammonium head-groups. The concentration of TTAC has a similar but smaller effect on the size of the aggregate, $N_D$ increases in about 12 units with an increase of about 4% in the concentration of TTAC. The tendencies observed in the quadrupole splittings of decanol and chloride with the modifications in the composition of the solution are consistent with an increment in the size of the aggregate, both increase with increasing concentrations of decanol, TTAC and NaCl.

Table 2 shows the aggregation numbers, $N_D$, measured for 15 selected samples of the TTAB mesophase, as a function of solution’s composition. An analysis of the data in Table 2 shows that modifications in the composition of the mesophase have no clear effect on the measured $N_D$. The observed larger errors associated to $N_D$ in TTAB are attributed to the quenching of pyrene’s fluorescence by the high concentration of bromide ion.

A dynamic light scattering study about salt effects on the size of vesicles made of dioleoylphosphatidylglycerol (DOPG) and dioleoylphosphatidylcholine (DOPC) was published [22]. At low ionic strength the radius of the vesicle decreased with salt concentration; however, at high ionic strength, such as in our system, an increase in size with ionic strength was observed. They also reported that vesicles made of DOPG in NaCl were always larger than made in NaBr.

The fact that the TTAC aggregate is always bigger than the TTAB aggregate strongly suggests that the origin of the differences between both mesophases, regarding the quadrupole splittings of water and decanol, arises from differences in the dynamics of the interfaces. In effect, the observed differences can be attributed to different dissociation degrees from their respective counterions. A different interpretation of the results can be provided based on the existence of undulations; however, as discussed later, undulations can be completely discarded in this discotic nematic lyomesophases. Since the only difference between both mesophases is the nature of the counterion, these observations reveal the extremely important role of electrostatic interactions on the dynamics of these systems, particularly the interface. A deeper knowledge about the affinity of the interface for the different counterions appears necessary for a better understanding of these mesophases. Further experiments and molecular dynamics calculations were carried out to test this hypothesis, and the results are presented in the companion paper.

The CMC, aggregation number, dissociation degree and other properties of spherical micelles made of CTAC and CTAB in aqueous solutions have been recently revised using different techniques [23]. The results indicate that CTAC is more dissociated than CTAB, as proposed in this work.

A possible origin for the dissimilarities between both liquid crystal solutions is the difference in ionic radius of the cation. The ionic radius of chloride is about 0.14 Å bigger than the radius of bromide. This makes the electrostatic potential of bromide smaller and the water solvation shell less attached to it. A photoelectron spectroscopy study on the electrostatic stabilization energy of halide ions by water clusters of different sizes shows that for clusters of 1 to 6 water molecules, the solvent electrostatic stabilization energy of the ion is always greater for chloride than for bromide. Furthermore, the difference increases from 20 kJ/mol for a one water molecule cluster to 60 kJ/mol for a six water molecules cluster [24]. Therefore, the more weakly solvated counterion, bromide in this case, should have a closer approach to the surface formed by the ammonium head groups. Another possible reason for this marked preference could arise from the greater polarizability of bromide compared to chloride. For instance, the value of the longitudinal component of the polarizability tensor increases by 11.86 bohr$^3$ on going from NaCl to NaBr and increases by 9.64 bohr$^3$ on going from LiCl to LiBr, an increment of more than 30% in both cases [25]. The importance of the polarizability and ionic radii of chloride and bromide in water cluster solvation properties has been theoretically studied in detail using molecular dynamics simulations [26]. These authors concluded that ions with higher polarizability and ionic radii reside near the surface of water clusters, whereas smaller size and polarizability ions remained fully solvated at the interior of the cluster. The effects of halide ions on the structure of water have been also studied experimentally [27]. It was found that chloride presents a cosmotropic effect on the structure of water, whereas bromide shows a chaotropic behavior. Therefore, all the results seem to indicate that, in the case of the studied mesophases, bromide has the tendency to escape from the bulk water and be displaced to-
ward the interface and chloride prefers to be solvated in the bulk aqueous phase. Chloride prefers high water density regions and bromide prefers low water density regions.

5. Conclusions

The dynamic fluorescence quenching is a convenient methodology to measure the aggregation number of these mesophases. The sizes of the aggregates have been determined to be about 250 for TTAB, 300 for TTAC and 236 for SDS. These results are in agreement with reported values of the axis ratio, $\rho$, using different techniques [20,21], and allow discarding a previous estimation of a significantly bigger SDS aggregate [10].

Particles of this size cannot experience the undulations observed in lamellar mesophases [28,29]. Assuming the upper and lower limits of the undulating wavelength as 1000 nm (IR) and 300 nm (UV), both values are about 2 orders of magnitude bigger than the radius of the disk.

In this systems, chloride as counterion seems to induce aggregation, whereas bromide apparently does not. This is in agreement with previous observations in micelle solutions and follows the Hofmeister series [30].

Apparently, in TTAB the interface is significantly more neutralized than in TTAC, as predicted by the Hofmeister series, making the TTAB aggregate more rigid. The ammonium–ammonium electrostatic repulsions in TTAC increase the mobility of the interface components. A more neutralized interface, as in TTAB, provides a stronger electric field, which is able to align enough water electric dipole moments to give rise an observable quadrupole splitting. Further work to test this hypothesis is presented in the companion paper.

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