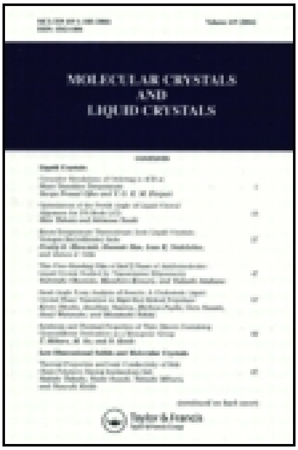

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Gojmir Lahajnar , Slobodan Zumer , Marija Vilfan , Robert Blinc & Leonard W. Reeves (1984): Pulsed Gradient NMR Diffusion Study in Lyotropic Nematics, Molecular Crystals and Liquid Crystals, 113:1, 85-92

To link to this article: http://dx.doi.org/10.1080/00268948408071673

Mol. Cryst. Liq. Cryst., 1984, Vol. 113, pp. 85-92
0026-8941/84/1134-0085/$15.00/0

Printed in the United States of America

PULSED GRADIENT NMR DIFFUSION STUDY IN LYOTROPIC NEMATICS

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Abstract. The translational diffusion of amphiphile molecules in lyotropic nematic phases has been studied for different orientations of the pulsed magnetic field gradient using the magic angle NMR spin–echo technique. Unrestricted diffusion was observed along the long axis of the cylindrical micelles and in the plane of the discotic micelles whereas in directions perpendicular to the above orientations diffusion was too small to be detectable. The observed magnitude of the diffusion coefficients as well as their anisotropy are characteristic for lamellar and hexagonal phases but the finite alignment times favour the view that the two mesophases are composed of finite micelles.

1. INTRODUCTION

Lyotropic nematic phases which are aqueous solutions of anisotropic micellar aggregates formed by amphiphilic molecules, exhibit long–range orientational order but no long–range translational order[1,2]. These phases are intermediate between the viscous, positionally ordered (lamellar, cubic or hexagonal) phases and totally disordered (isotropic micellar) phases. The first lyotropic nematic mesophase was found in the system sodium decylsulfate/1–decanol/water and sodium sulfate[3]. Since then many other aqueous solutions of amphiphilic compounds have been found to exhibit the lyotropic nematic behaviour[1].

In order to throw additional light on the problem of molecular structure and dynamics, and in particular on the size and shape of micelles, we decided to perform the measurements of the diffusion coefficient in two lyotropic nematic liquid crystalline mesophases: one composed of finite rod–shaped or cylindrical micelles (CM), and another composed of finite disc–shaped micelles (DM) of bilayer thickness. Both types exhibit positive anisotropy of the diamagnetic susceptibility ($\Delta\chi > 0$), inferring the spontaneous average alignment of micellar symmetry axes along the static magnetic field B_o [4–6]. To determine the diffusion coefficient of the system a pulsed magnetic field gradient NMR spin–echo (PGSE NMR) technique was used [7]. This technique can be applied for the study of nematic lyotropic phases because of spontaneous alignment of the micellar directors along the B_o direction and long orientational relaxation time.
A fast reorientation of the aligned samples to the magic angle (54.7°) with respect to the B_o direction namely reduces the interproton dipolar interactions, T_2 becomes longer and the spin–echo signal can be observed [8–11]. Attenuation of the echo amplitude due to translational diffusion of molecules is then given by [7]

$$A(G)/A(0) = \exp[-\gamma^2 G^2 D\delta^2 (\Delta - \delta/3)] \quad , \tag{1}$$

where G and δ are, respectively, the amplitude and width of the magnetic field gradient pulses, Δ is the diffusion time defined by the time separation of the gradient pulses in the sequence, γ is the magnetogyric ratio, and D the translational diffusion coefficient of amphiphile molecules. D is determined as a ratio $\ln[A(G)/A(0)]/$ $/\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$. The diffusion is unrestricted if D does not depend on δ.

2. EXPERIMENTAL

The samples of CM and DM lyotropic nematic mesophases were prepared in the laboratory of Prof. Reeves. The CM lyotropic nematic mesophase was obtained by mixing potassium laurate, KCl and D_2O, in the mole ratio 1.000 : 0.288 : 23.42. The DM mesophase was obtained by mixing of potassium decanoate, potassium heptyloxybenzoate, KCl, decanol and D_2O, in the mole ratio 0.8 : 0.200 : 0.693 : 0.279 : : 19.7. Both mesophases which are nematic at T = 30°C exhibit the property of spontaneous alignment of micellar symmetry axes along the static magnetic field B_o ($\Delta\chi > 0$). The alignment time in a field $B_o \cong 1{,}4$ Tesla at 30°C is about 1 hour for the CM mesophase, and more than 1 hour for the DM mesophase[6]. PGSE NMR diffusion measurements were performed on a Bruker B – KR 322 s pulsed spectrometer at the proton resonance frequency $\nu_H = 57$ MHz. A special homemade diffusion attachment was used. Before each application of gradient pulses, the aligned sample was rotated around the normal to the magnetic field so that there was a magic angle (54.7°) between the micelle director ($\vec{n}$) and the vector $\vec{B}_o$. At this orientation the amplitude of the spin–echo was observed by the usual $\pi/2 - \pi$ rf pulse sequence. The angular independent part of the spin – echo signal corresponds to the residual HOD protons in the D_2O solvent. The PGSE NMR method[7] was applied, with fixed amplitude (G = 530 gauss/cm) of the gradient pulses and fixed diffusion time Δ of 3 msec dictated by the magic angle amphiphile proton T_2, whereas the width δ of the G pulses was varied between 0 and 1.8 msec. The temperature of the sample was kept constant at T = 30 ± 0.2 °C.

3. RESULTS AND DISCUSSION

Diffusion of the HOD molecules was studied by the application of relatively narrow gradient pulses ($\delta \approx 0 - 0.3$ msec). The corresponding diffusion coefficient D_{HOD} is found to be independent of the diffusion time Δ in the measured interval $\Delta = 2 - 20$ msec, but exhibits some angular dependence. For the DM type sample $D_{HOD}(\vec{G} \perp \vec{n}) = 1.0 \times 10^{-5}$ cm^2/sec and $D_{HOD}(\vec{G} \parallel \vec{n}) = 0.7 \times 10^{-5}$ cm^2/sec. In the CM sample the angular dependence of D_{HOD} may be neglected in the limit of experimental error (± 7 %), and the average value is $D_{HOD} = 1.2 \times 10^{-5}$ cm^2/sec. For comparison, the corresponding value of D_{HOD} in pure D_2O at 30°C is 2.1×10^{-5} cm^2/s[12]. The HOD contribution to the echo is effectively suppressed when $\delta \gtrsim 0.5$ msec at $\Delta = 3$ msec.

As far as the diffusion of amphiphile molecules inside the micelles is concerned, observations were made at $\vec{G} \parallel \vec{n}$ and $\vec{G} \perp \vec{n}$, with $\vec{n}$ oriented to the magic angle with respect to $\vec{B}_0$. If $\vec{G}$ was parallel to $\vec{n}$ in the CM sample, the fast initial echo attenuation due to HOD protons was followed by the much slower decay due to amphiphile protons (Fig. 1a). However, for $\delta > 0.8$ ms the plot $\ln[A(G)/A(0)]$ against $\delta^2(\Delta - \delta/3)$ was a straight line (as it was for $\delta < 0.3$ ms), indicating unrestricted diffusion for effective diffusion times $\Delta_{eff} = \Delta - \delta/3 \leqslant 2.4$ ms. From the slope the diffusion coefficient $D_{CM} = 4.2 \times 10^{-7}$ cm^2/sec was determined. On the other hand, when $\vec{G}$ was perpendicular to the $\vec{n}$ direction, *no* measurable attenuation of the amphiphile part of the spin—echo was observed. So there is no observable amphiphile diffusion in the direction normal to the cylinders.

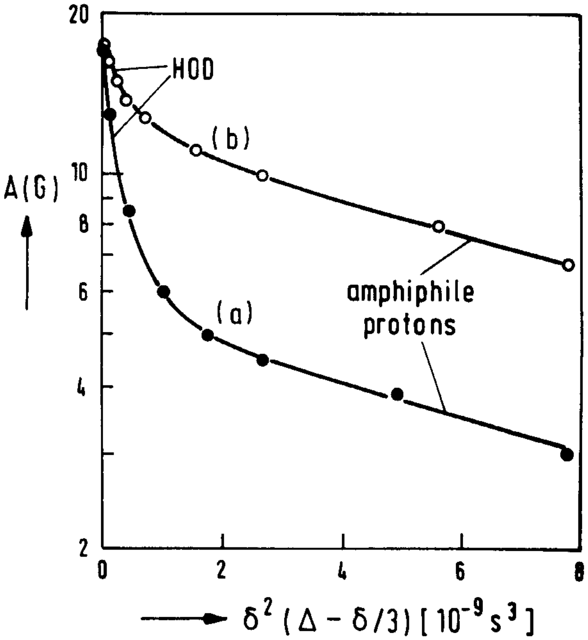

FIGURE 1. Proton NMR spin—echo attenuation (a) in the CM phase ($\vec{G} \parallel \vec{n}$, $\sphericalangle\ \vec{n}, \vec{B}_0 = 54.7^\circ$) and (b) in the DM phase ($\vec{G} \perp \vec{n}$, $\sphericalangle\ \vec{n}, \vec{B}_0 = 54.7^\circ$).

The behaviour of the DM sample is quite similar. For $\vec{G} \perp \vec{n}$ (i.e. $\vec{G}$ in the disc plane), the remaining slow echo attenuation again yielded a straight–line plot ln [A(G)/A(0)] vs $\cdot\delta^2(\Delta - \delta/3)$, corresponding to the unrestricted diffusion (for $\Delta_{eff} \leqslant 2.4$ ms) with $D_{DM} = 3.7 \times 10^{-7}$ cm^2/sec (Fig. 1b). However, for $\vec{G} \parallel \vec{n}$, *no* observable echo attenuation of the amphiphile part could be observed, what means that there is no observable diffusion in the direction normal to the disc planes. There are two possible interpretations of our data:

(i) Intramicellar diffusion. The observed molecular diffusion exhibits complete anisotropy indicating the existence of a perfect orientational order of the sample. Together with the fact that one– and two – dimensional diffusion processes are unrestricted, this is a characteristic feature of hexagonal and lamellar phases. The magnitude of diffusion coefficients are as well quite close to the values quoted for the hexagonal and lamellar phases[9–11,13]. On the other hand, however, finite alignment times ($\geqslant$ 1 hour) exclude the possibility of mono-domain lamellar or hexagonal phases. Taking into account the fact that our diffusion measurements are limited to the diffusion time interval $\Delta_{eff} \approx 2$ ms we can estimate the lower limits for characteristic extensions of the aggregates. The minimum length of the cylindrical aggregate is given by

$$\ell_{min} = \sqrt{2\, D_{CM}\, \Delta_{eff}} \approx 0.4\ \mu m \quad , \tag{2}$$

and similarly the minimum diameter of the planar aggregate is given by

$$d_{min} = \sqrt{4\, D_{DM}\, \Delta_{eff}} \approx 0.5\ \mu m \ . \tag{3}$$

In view of these facts our samples can be CM and DM nematics composed either of aggregates whose lower size is several tenths of μm, or polydomain hexagonal and lamellar phases characterized by a similar domain size.

The unrestricted diffusion in micellar nematics could be in principle partly due to the exchange of molecules between different micelles. This process occurs when two neighbouring micelles fuse. Nevertheless, for such an exchange it is hard to expect complete anisotropy and practically the same diffusion rate as for the intramicellar case.

(ii) Micellar diffusion. Here we assume that the measured diffusion coefficients correspond to the diffusion of micelles as whole entities. In order to relate the diffusion coefficient to the viscosity of the medium and to the dimension of micelles, we use a slightly modified Einstein relation

$$D \approx \frac{kT}{\eta}\frac{h}{2S} , \tag{4}$$

which approximately takes into account the presence of many micelles separated by the water layers of thickness h. Here k is the Boltzmann constant, T is the sample temperature, η is the viscosity of the medium, and S is an average surface of a micelle. For η we take pure water data ($\eta \approx 10^{-3}$ kg/ms) and for the water layer thickness we use the data of Hendrikx and Charvolin[14]: h $\approx$ 1.8 nm in the DM case and h $\approx$ 1.1 nm in the CM case. The diameter of the cylindrical micelle and the width of the discotic micelle are taken to be 2.6 nm and 1.9 nm, respectively. Thus, inserting our diffusion data into Eq. (4) and expressing the obtained corresponding effective surfaces in terms of the characteristic micellar extensions, we find $\ell \approx 7$ nm for the cylinder length and d $\approx$ 8 nm for the disc diameter. These estimated micellar sizes are similar to those obtained by the small angle X–ray scattering[14], but in view of such a small shape anisotropy ($\sim$3 to $\sim$ 4) they cannot explain the observed complete anisotropy of the diffusion process.

4. CONCLUSION

The translational diffusion in lyotropic nematic phases with disc–like and rod–like micelles has been studied by the PGSE NMR method. The property of spontaneous alignment of the samples in the external magnetic field B_0 was essential for this approach since it was the magic angle (54.7°) orientation of the micellar directors that enabled to lengthen the amphiphile proton T_2 enough that the NMR spin–echo could be formed. We found an unrestricted diffusion along the axis of cylindrical micelles and in the plane of discotic micelles, but *no* observable diffusion in perpendicular directions, respectively. The observed anisotropy and magnitude of the diffusion coefficients are characteristic for diffusion in lamellar and hexagonal phases, but finite alignment times of the two mesophases favour the view that we are dealing with finite micelles. The data indicate typical extensions of ~ 0.4 μm in the CM case and ~ 0.5 μm in the DM case. Such a structure cannot be distinguished from a hexagonal or a lamellar polydomain phase containing domains of similar sizes.

On the other hand, an alternative explanation of our results in terms of the micellar diffusion in aqueous medium requires disc diameters of ~ 8 nm and cylinder lengths of ~ 7 nm. If it is assumed[14] that the width of the discs is ~ 1.9 nm and the diameter of the cylinders ~ 2.6 nm, such a small shape anisotropy (~ 3 to ~ 4) cannot explain the observed strong anisotropy of the micellar amphiphile diffusion.

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