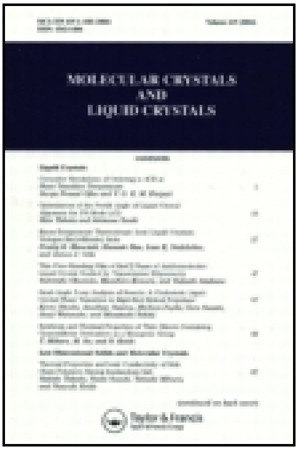

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Proton Spin Relaxation in the Rod Micelles of Type I CM Mesophases

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Proton Spin Relaxation in the Rod Micelles of Type I CM Mesophases

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The dynamics of the hydrocarbon chains in lyotropic nematic type I cylindrical micellar liquid crystals prepared with D_2O has been selectively studied by Zeeman and rotating frame nuclear spin-lattice relaxation. The measurements of the proton spin-lattice relaxation time T_1 as a function of frequency and temperature demonstrate that relatively fast local fluctuations of individual amphiphilic chains relax the proton spins at high magnetic fields. This process is facilitated also by the rapid diffusive motion of the chains within the micellar units. The rotating frame Zeeman relaxation time T_{1x} is associated at room temperature with a long correlation time of ~11 μs. Slow micellar orientational fluctuations have been assigned to this characteristic time.

INTRODUCTION

Type I CM[1,2] lyotropic mesophases consist of finite cylindrical micelles disposed with orientational order in an aqueous matrix. In special situations in narrow capillaries, positional order can be detected,[3] but the mesophase can be regarded as nematic with large cylindrical micelle units of 500–2500 Å in length as the building units of the structure.[4,5] Type I signifies positive diamagnetic susceptibility anisotropy[6] which leads to homogeneous alignment of the director parallel to the static magnetic field in NMR spectrometers. The Type I CM mesophase is related to the H_α hexagonal phase, also Type I,[7] where the cylinders become extremely long and crystallize out with hexagonal positional order perpendicular to their axes. The analysis of the degree of order profiles obtained from deuterium magnetic resonance of deuteriated hydrocarbon chains, shows that the packing of individual chains in the finite micelles does not differ from that of the hexagonal phase[5] but that a large decrease in order between H_a and Type I CM mesophases in thermodynamic equilibrium can be associated with the motion of the finite micelles.[5] This cooperative motion of between 10^4 and 10^5 amphiphiles will necessarily have a much larger correlation time than any motion of individual amphiphile units of the micelle. In this respect the present study is devoted to proton relaxation measurements including a probe of the low field $T_{1\rho}$ which is sensitive to longer correlation times. The nature of the Type I CM phases allows the director to be rotated at fixed angles to the static field and relaxation measurements performed as a function of this angle.[8] Proton spin relaxation times and their temperature and frequency dependence were studied by McLachlan, Natusch and Newman[9] using the mesophase first reported by Flautt and Lawson.[10] There was continuity in the values across two phase changes, indicating certainly that the dominant mechanism of relaxation was the result of rapid motions at the molecular level. The mesophase composition reported[9] indicates that it was a Type II DM with $\Delta\chi < 0$ but we have previously shown that very small misweighings of decanol content or hydrolysis can lead to a two phase lamellar/Type II DM system.[11] These early measurements[9] were made therefore on a system which was not Type I CM and no angular experiments were reported.

The X-ray diffraction on Type I CM mesophases were made by Amaral[3] and co-workers and Charvolin[12] *et al.*

EXPERIMENTAL AND RESULTS SECTION

Nematic phases were prepared with the following compositions: (a) Lithium decyl sulphate 28.7 wgt%, decanol 8.2% and D_2O 63.1%; (b) Sodium decyl sulphate 35.3%, decanol 7.1% and D_2O 57.6%. These compositions correspond to Type I CM behavior.

Measurements of relaxtion times T_1 were made using a Bruker SXP pulsed NMR spectrometer. T_{1x} and $T_{1\rho}$ were measured with a Spin-lock Electronics spectrometer. All measurements were made at T = 30°C. In addition a temperature dependence of the proton T_1 was measured.

(a) Measurements of proton-spin relaxation time

The studies were made on a mesophase (b) (Type I CM) sample described in the experimental section. The hydrocarbon chain segments in the system originate from two amphiphiles, decanol and decylsulphate, but the former is in low concentration so that relaxation effects have been associated with the decylsulphate chains. Electrical conductivity and specific inductive capacity measurements were made during the period of orientation in the magnet of 10^4

G strength. These measurements indicate that an aligned sample is obtained in about 1 hour at this field strength. The samples have a negative dielectric and conductivity anisotropy.[13]

The nuclear spin-relaxation in nematic liquid crystals, in contrast to isotropic liquids, is normally frequency dependent.[14] The frequency dependence may be due to local nematic order fluctuations in thermotropic liquid crystals and/or the modulation of intermolecular dipolar interactions by translational self diffusion.[15] In the present case the order fluctuations correspond to motions of the hydrocarbon chains aligned in the large micelles. It is the motion of the micelles which lead to local nematic order fluctuations in the Type I CM liquid crystals and this has a much larger correlation time. In so far as the hydrocarbon chains are aligned in a bilayer structure[1] they have independent motions such as trans/gauche rotations, cone motion as rigid bodies and the motions associated with their anchoring in the interface of the micelle. Such motions are effective in coupling to the nuclear spin system. The local fluctuations arising from the order director fluctuations, including the contribution due to the diffusion effects will produce a frequency dependence[14]

$$\frac{1}{T_1} = A\omega_L^{-1/2} + B. \tag{1}$$

In Figure 1 the values of proton T_1's for a fully oriented (Type I) mesophase of sodium decyl sulphate/decanol bilayers (Sample b of experimental section) are shown to obey the relationship (1) with $B \sim 0$. The implication of this ob-

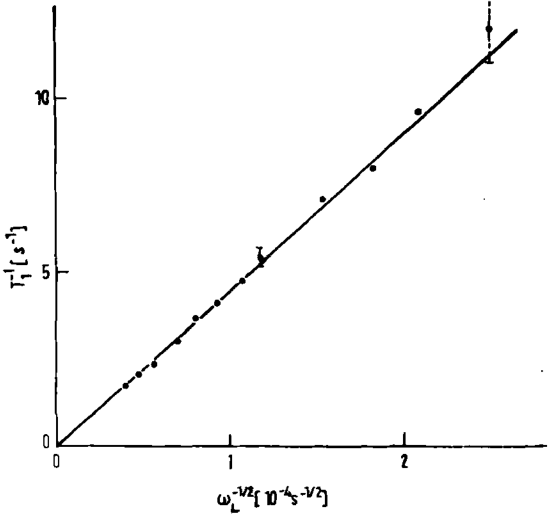

FIGURE 1 T_1^{-1} plotted vs $\omega_L^{-1/2}$ for protons in the hydrocarbon chains of the cylindrical finite micelles of a type I nematic phase. Material is of type (b) described in the experimental section.

servation is that local order fluctuations of the aligned chains relax the spin system at high fields. Relaxation by fast diffusion modulating the intermolecular dipolar interaction—which would contribute to B only—is weak if not negligible (since $B \simeq 0$). There is also no evidence of a slow diffusion rate proportional to ω_L^{-2}. Since the experimental frequency range 60–4 MHz is rather small, it can be proposed only that the local order fluctuation is the main source of the Zeeman relaxation at high fields.

There is a strong temperature dependence of T_1 for this sample, which yields an activation energy 0.23 eV.

(b) Measurements of proton rotating frame relaxation time

Measurements of T_{1x} and $T_{1\rho}$ have been made using the two pulse spin-locking method[16] at a Larmor frequency of 17.6 MHz. The magnetization which follows the spin locking pulse, under the condition of strong Zeeman-dipolar mixing, is:

$$M_x = M_o \frac{H_1^2}{H_1^2 + H_L'^2}. \tag{2}$$

M_o is the equilibrium magnetization of the spin system, H_1 is the magnitude of the rotating field and H'_L is the proton local field in the rotating frame.[17] This relation was used to evaluate H'_L which was found to be 0.25 G. The sample was a Type I CM mesophase fully aligned along the static magnetic field, but with 10% of the sodium decylsulphate substituted by lithium decyl sulphate. This procedure produces a Type I CM liquid crystal which re-aligns very slowly in the static field.[6,18] The velocity of re-alignment was slow enough to allow measurements of $T_{1\rho}$ as a function of the angle Ω.

The relaxation in the rotating frame was measured at low H_1, where the Zeeman and dipolar reservoirs are strongly coupled, and at high H_1. At high H_1 the pure Zeeman relaxation rate T_{1x} is measured. It is proposed that the relaxation is a sum of a frequency ($\omega_1 = \gamma H_1$) dependent rate and a "white" rate D. We then have

$$T_{1x}^{-1} \sim \frac{C\tau}{1 + \omega_1^2\tau^2} + D, \tag{3}$$

with C measuring the strength of the slow fluctuating dipolar field due to order director fluctuations. The contribution D is a sum of a fast order fluctuation relaxation, a diffusion rate and possibly some other mechanism, which is too slow to contribute to T_1 but is "white" in the rotating frame. It was observed that the first term is dispersive in the H_1 region from 10 to 5 G. At higher H_1 it becomes $C/\tau\gamma^2 H_1^2$. Its low field limit is $C\tau$. In Figure 2 T_{1x}^{-1} is plotted versus H_1^{-2}. The slope $C/\gamma 2\tau$ is 300 sec^{-1}G^2 and the intercept D is 18 sec^{-1}.

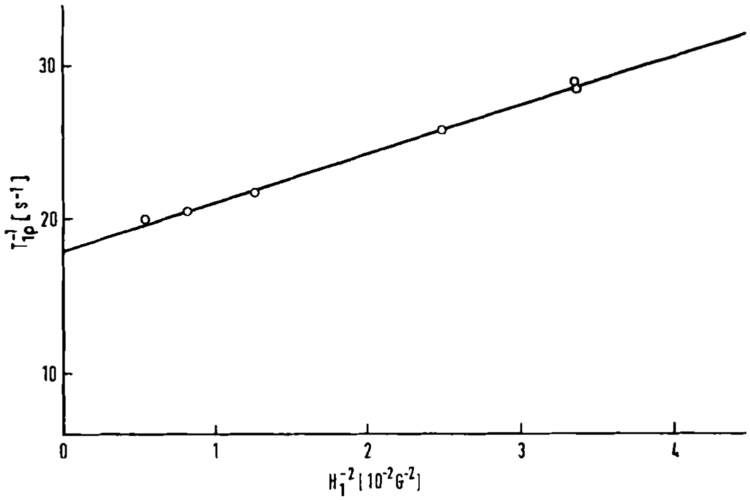

FIGURE 2 The plot of the proton relaxation rate T_{1x}^{-1} versus H_1^{-2} in the high H_1 region.

At low H_1 the observed relaxation rate $T_{1\rho}^{-1}$ is a weighted average of a Zeeman (T_{1x}^{-1}) and a dipolar (T_{1D}^{-1}) rate[16]

$$T_{1\rho}^{-1}(H_1^2 + H_L'^2) = T_{1x}^{-1}H_1^2 + T_{1D}^{-1}H_L'^2 \tag{4}$$

It is convenient to introduce the reduced field $H_r = H_1/H_L'$ and divide the Eq. (4) by $H_L'^2$. The so called spin thermometric equation is obtained:[17]

$$T_{1\rho}^{-1}(H_r^2 + 1) = T_{1x}^{-1}H_r^2 + T_{1D}^{-1}. \tag{5}$$

Since T_{1x}^{-1} is "white" at low H_1, where Eq. (5) holds, it is possible to simplify Eq. (5) as follows:

$$T_{1\rho}^{-1}H_r^2 = (C\tau + D)H_r^2 + T_{1D}^{-1}. \tag{6}$$

A plot of Eq. (6) is shown in Figure 3.

From the low field experiment, Figure 3, the slope $(C\tau + D)$ of 45 sec^{-1} and the intercept $T_{1D}^{-1} = 55$ sec^{-1} are obtained. The value of T_{1D}^{-1} is rather large indicating that a very slow motion relaxes the dipolar reservoir. From the slope of 45 sec^{-1} the value for D obtained in the high field experiment, is subtracted. The resulting value for $C\tau$ is 27 sec^{-1}. From $C\tau$ and $C/\gamma^2\tau$ the correlation time τ for the slow order director fluctuation which makes T_{1x} dispersive, is calculated to be 11 ± 4 μ sec. Director fluctuations are thus contained in Eq. (3) in terms $C\tau/(1 + \omega_1^2\tau^2)$ and the fast fluctuations in D. The slow rate is characterized by a correlation time of 11 μ sec which makes T_{1x} dispersive in the region of small H_1.

The value measured for $T_{1\rho}$ depends upon the time that the sample remains

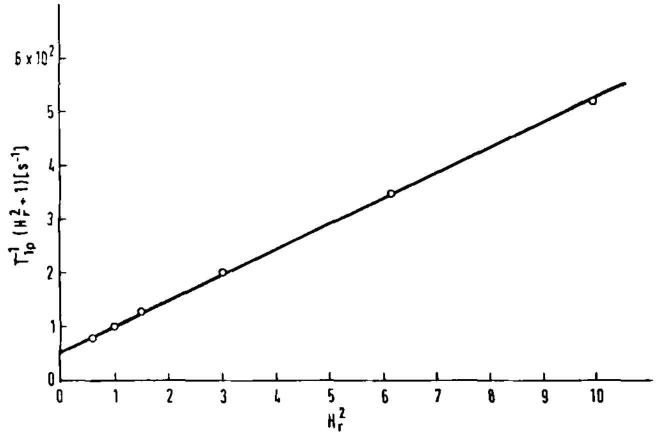

FIGURE 3 The plot of $T_{1\rho}^{-1}(H_r^2 + 1)$ versus H_r^2 for protons in the low H_1 region.

immersed in the static magnetic field. Initially the alignment of the directions is random, leading to a powder diagram line shape.[8] After a period of ~2 hours in the field the directors are uniformly aligned along the magnetic field.[4] The $T_{1\rho}$ observed on first immersion in the static field is a mean for all Ω. As the time passes the $T_{1\rho}$ value approaches ~50 m secs, characteristic for the parallel alignment of directors to the field ($\Omega = 0$). The sequence of $T_{1\rho}$ values as a function of time in the magnetic field is plotted in Figure 4.

The aligned sample can be rotated from the static magnetic field direction ($\Omega = 0$) to point to any direction Ω. This allows measurements of the $T_{1\rho}$ ani-

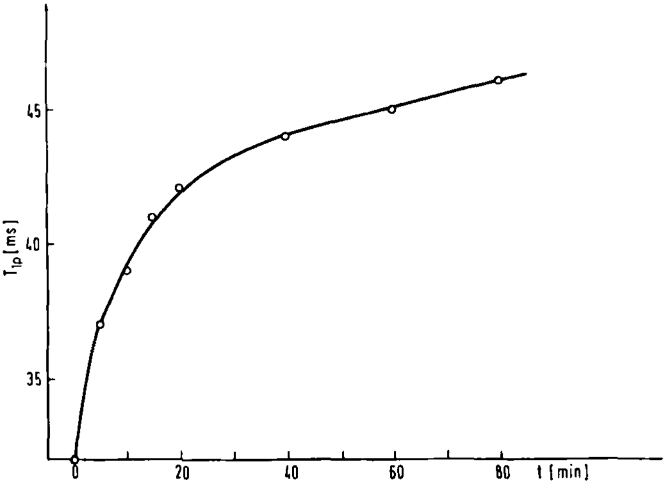

FIGURE 4 Proton $T_{1\rho}$ during the period of sample alignment in the magnetic field.

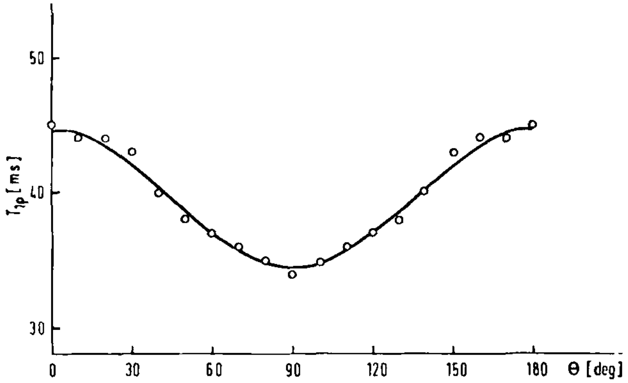

FIGURE 5 The dependence of the proton $T_{1\rho}$ for an aligned sample on the angle Ω between the director and the static magnetic field direction.

sotropy. $T_{1\rho}$ as a function of Ω is plotted in Figure 5. The solid line is the best fit to the experiment. This angular dependence has been observed in a low field at 2 ± .5 G. Because of this, the observed anisotropy may be partially the result of the anisotropy of H'_L. In other words, the dipolar specific heat varies with Ω and as a consequence the rate $(T_{1\rho}^{-1})$, which is common to the Zeeman and the dipolar energy reservoir, varies with Ω. However, in addition, both T_{1x} and T_{1D} may be anisotropic by themselves. The anisotropic order fluctuation rate (in T_{1x}) may be partially or to a large degree, responsible for the observed anisotropy of $T_{1\rho}$. A detailed study of this anisotropy is underway.

The T_1, associated with the high frequency correlation time process, shows no angular dependence within the limits of experimental error.

DISCUSSION

(a) The structural basis of the mesophase

The aligned mesophases studied here are exclusively Type I CM $\Delta\chi > 0$.

Although the NMR evidence is not entirely conclusive in structural terms,[1] the recent evidence of low angle X-ray diffraction on these mesophases,[11,12] does give confirmation of the structure. The Type I CM system can show some positional order of the micelles in narrow capillaries, but in NMR tubes of much larger diameter the positional order, which decreases in intermediate sized tubes is presumed to be absent giving a truly nematic arrangement of micelles.[7] The sign of the dielectric and conductivity anisotropy is not immediately explainable in terms of the above model.

There are two important levels of structure, that of amphiphile packing in the micelles and the long range orientational order of the micelles themselves.

The physical properties of dielectric constant, conductivity and $T_{1\rho}$ measured here, vary regularly as the sample is aligned by the field. This has been illustrated in the results section.

(b) Longitudinal relaxation times of chain protons

The behavior of the proton nuclear spin relaxation T_1 in the high static field is understandable in the above structural terms. The long finite cylindrical micellar units of the structure are similar in the internal amphiphile packing with the closely related H_α hexagonal mesophase, which has two positional degrees of order of infinite cylinders.[1] The results of T_1 for the hydrocarbon chains, at different frequencies and at varied temperatures confirms this close similarity. The correlation time of the order of $\sim 10^{-9}$ to 10^{-10} sec is associated with diffusive an internal trans/gauche motion of chains in analogy to the situation in the L_α lamellar mesophases studied by Charvolin *et al.*[19] The difference in geometry between the cylindrical and the lamellar shape of the bilayers should not be significant in this relaxation process. The nuclear spin relaxation of protons in the chain at the high static fields is dominated by a time dependent process associated with order fluctuations of individual amphiphile chains and their motions within the cylindrical micelle units. These processes are not significantly dependent on the angle between the director and the magnetic field.

(c) Relaxation of chain protons in the rotating frame

Two features of the rotating frame relaxation are noteworthy in the structural model. The long correlation time of 11 μs must be associated with co-operative motions of many hydrocarbon chains, because all other processes such as trans/gauche rotations in segments, self-diffusion, chain rotation, etc. have correlation time which are orders of magnitude shorter at room temperature. The only co-operative motions of chains possible within the structural model are the motions of the micelle unit in the aqueous matrix. The assignment of this correlation time to overall micelle oscillations is therefore made.

Acknowledgments

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