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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Luckhurst, G. R. , Sugimura, A. , Timimi, B. A. and Zimmermann, H.(2005) 'NMR determination of the physical properties of nematics', Liquid Crystals, 32: 11, 1389 — 1396

To link to this Article: DOI: 10.1080/02678290500124692

URL: http://dx.doi.org/10.1080/02678290500124692

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Liquid Crystals, Vol. 32, No. 11–12, November–October 2005, 1389–1396

NMR determination of the physical properties of nematics

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(*Received 3 December 2004; accepted 11 January 2005*)

Certain physical properties of nematics can be obtained from the field-induced static and dynamic director orientations in thin films. Here we describe how deuterium nuclear magnetic resonance (NMR) spectroscopy can be used to investigate the field-induced director orientation in nematic liquid crystals. This powerful approach is illustrated with specifically deuteriated 4-pentyl-4′-cyanobiphenyl (5CB) subject to the magnetic field of the spectrometer and an electric field applied at an angle to it. A series of deuterium NMR spectra was acquired as a function of the applied electric field, which can be used to explore the static director orientation. When the electric field is applied to the nematic, the director moves from being parallel to the magnetic field to being at an angle to it (the turn-on process) because $\Delta\tilde{\varepsilon}$ and $\Delta\tilde{\chi}$ are both positive for 5CB. After the electric field is switched off, the director relaxes back to being parallel to the magnetic field (the turn-off process). Deuterium NMR spectra were recorded during the turn-on and the turn-off alignment processes as a function of time. Analysis of these results for the static and dynamic experiments, based on the predictions of continuum theory, provides the physical properties of the nematic.

1. Introduction

There have been many investigations of the alignment of nematic liquid crystals by a magnetic and/or an electric field. There have also been studies of the effect of applying two constraints to a nematic sample, such as an electric field and a surface torque. As a result, the basic features of these hydrodynamic processes have been characterized for the systems in their equilibrium and non-equilibrium states. To complement the experiments, theoretical models based on continuum theory have been developed, which successfully describe these phenomena [1].

Such macroscopic behaviour has been investigated with nuclear magnetic resonance (NMR) spectroscopy. For example, the effect of an electric field on the NMR spectra of a nematic resulting from a change in the director orientation was first demonstrated using proton NMR [2]. More recently, deuterium NMR has been widely used in the investigation of liquid crystals, primarily because the deuterium NMR spectra of specifically or fully deuteriated materials are simple, especially when compared with their proton analogues [3]. The quadrupolar splittings observed in the spectra are related, amongst other things, to the angle made by the director with the magnetic field. In consequence, deuterium NMR spectroscopy is expected to be a powerful method with which to investigate the director orientation and its distribution [4–21]. The static [9, 10] and dynamic [11–17] director orientation in thin films of 4-pentyl-4′-cyanobiphenyl (5CB), and 4-octyl-4′-cyanobiphenyl (8CB) [18–21], have been widely studied with deuterium NMR spectroscopy.

In this paper, we describe the determination of nematic physical parameters given by the static and dynamic director orientations in thin nematic liquid crystal films subject to competing homogeneous constraints. The nematogen used as an exemplar for our approach is 5CB and its director orientation, both static and dynamic, was determined using deuterium NMR spectroscopy. The electric field makes an angle with the magnetic field of the spectrometer. A series of deuterium NMR spectra was obtained as a function of the applied electric field, which could then be used to explore the static director orientation with the aid of the

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500124692

Zocher–Oseen–Frank continuum theory. When an electric field of sufficient strength is applied to the nematic film, the director moves from being parallel to the magnetic field to being at an angle with respect to it (the turn-on process) because $\Delta\tilde{\varepsilon}$ and $\Delta\tilde{\chi}$ are both positive for 5CB. After the electric field is switched off, the director relaxes back to being parallel to the magnetic field (the turn-off process). Time-resolved deuterium NMR spectra recorded during the turn-on and the turn-off alignment processes can be analysed in terms of the Leslie–Ericksen theory to give the field-induced director relaxation times. The static and dynamic NMR experiments then lead to the physical properties of the nematic phase.

The arrangement of this paper is as follows. In the next section we give the theoretical background to the NMR method and to the dynamic alignment of the nematic director subject to static magnetic and electric fields. In § 3 we describe the NMR experiments. The results of these are given in § 4 where they are discussed in the context of both continuum theory and the hydrodynamic theory for director dynamics. This analysis gives the ratio $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$, the diamagnetic anisotropy, $\Delta\tilde{\chi}$, the field-induced relaxation times and the rotational viscosity coefficient. The investigation is summarized in § 5, where we also give our conclusions.

2. Theoretical framework

Deuterium NMR provides a powerful technique with which to determine the director orientation in a liquid crystal and we now describe briefly the background to this. The nuclear spin of deuterium is one, so it possesses a quadrupole moment, which interacts with the electric field gradient at the nucleus to give a tensorial quadrupolar interaction. This does not influence the number of lines in the deuterium NMR spectrum for a normal liquid because the random and rapid molecular motion averages the quadrupolar interaction to zero. The NMR spectrum of a single deuteron, therefore, contains a single line composed of a pair of degenerate transitions. In a liquid crystal phase this degeneracy is removed because of the intrinsic long range orientational order combined with the quadrupolar interaction of the deuterium nuclei. For a monodomain sample, in which the director is uniformly aligned, the NMR spectrum consists of a single doublet as shown in figure 1. The separation, $\Delta\tilde{\nu}$, between the quadrupolar split lines is related to the long range orientational order of the molecules, but we shall not be concerned with this aspect here. Instead we concentrate on the dependence of the quadrupolar splitting, $\Delta\tilde{\nu}$, on the angle made by the director with the magnetic field of the NMR spectrometer. Now the quadrupolar splitting is given by [5]

$$\Delta\tilde{\nu}(\theta)=\Delta\tilde{\nu}_0 P_2(\cos\theta) \tag{1}$$

where $\Delta\tilde{\nu}_0$ is the splitting when the director is parallel to the magnetic field, θ is the angle between the director and magnetic field and $P_2(\cos\theta)$ is the second Legendre polynomial. As the director moves from being parallel to the field the splitting is predicted, and observed, to decrease, pass through zero at the magic angle ($\theta=54.74°$) and then to increase to one half of $\Delta\tilde{\nu}_0$, when the director is orthogonal to the magnetic field. Strictly, the quadrupolar splitting changes sign at the magic angle but the sign of the splitting is not directly available from the spectrum.

One of the prime advantages in using NMR spectroscopy to determine the director orientation is that the form of the spectrum is also influenced by the distribution of the director with respect to the magnetic field. In other words we can see from the spectrum whether the sample is a monodomain or not, and if not then the form of the director distribution can be determined given the aid of some theoretical prediction for the distribution function. This situation arises because when the director is not uniformly aligned the observed spectrum is a weighted sum of the spectra from all director orientations, provided the molecular diffusion between different director orientations is slow on the NMR timescale, which is usually the case.

Now that we have seen how deuterium NMR spectroscopy can be used to determine the director orientation with respect to the magnetic field, we shall consider the factors that influence this orientation. These factors include the electric and magnetic fields, surface forces and the elastic torques. In our experiments the strength and orientation of the electric field are varied to alter the director orientation and so

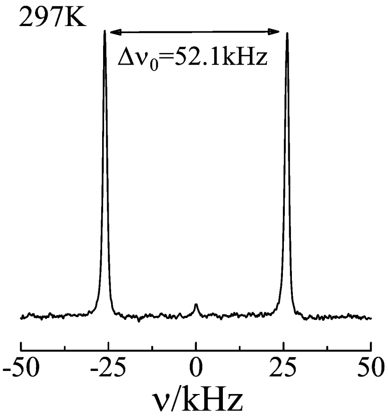

Figure 1. A typical deuterium NMR spectrum of 5CB-d_2 recorded at 297 K with no electric field; the quadrupolar splitting, $\Delta\tilde{\nu}_0$, is 52.1 kHz.

determine the properties of the nematic. Indeed it is possible to increase the electric field strength so that it overcomes the director alignment resulting from the magnetic field and surface force. To aid in the interpretation of the NMR spectra observed on varying the electric field, it is valuable to have some theoretical guidance as to the form of the director distribution and relaxation. For a monodomain director subject to both electric and magnetic fields, ignoring surface anchoring effects, which is a reasonable assumption for the untreated glass surfaces and cell thicknesses that we employ, the hydrodynamic theory gives the form of the director relaxation. We shall, therefore, now consider the Leslie–Ericksen-based theory [22] for the time dependence of the nematic director subject to both magnetic and electric fields.

Essentially all of the deuterium NMR spectra in our study are dominated by a single quadrupolar doublet, which allows us to determine the director orientation associated with a monodomain sample. In this analysis, therefore, we treat the director as being uniformly aligned. As shown in figure 2, the electric field makes an angle α with the magnetic field. The rate of change of the director orientation is given, for the turn-on process, by the torque-balance equation [23] which for a monodomain nematic [11] is

$$\gamma_1 \frac{\mathrm{d}\theta(t)}{\mathrm{d}t} = -\frac{\Delta\tilde{\chi}}{2\mu_0} B^2 \sin 2\theta(t) + \frac{\varepsilon_0 \Delta\tilde{\varepsilon}}{2} \mathbf{E}^2 \sin 2(\alpha - \theta(t)) \quad (2)$$

where γ_1 is the rotational viscosity coefficient, μ_0 is the magnetic permeability and ε_0 the dielectric permittivity of a vacuum. The solution of equation (2) is obtained analytically as [11]

$$\theta(t) = \theta_\infty + \tan^{-1}[\tan(\theta_0 - \theta_\infty)\exp(-t/\tau)] \quad (3)$$

where θ_∞ is the limiting value of $\theta(t)$ when t tends to infinity, τ is the relaxation time, and θ_0 is the initial angle. The limiting value θ_∞ is given by

$$\cos 2\theta_\infty = \frac{1 + \rho\cos 2\alpha}{(1 + 2\rho\cos 2\alpha + \rho^2)^{\frac{1}{2}}}, \quad (4)$$

where

$$\rho = \frac{U_\mathrm{E}}{U_\mathrm{M}} = \mu_0 \varepsilon_0 \left(\frac{\mathbf{E}}{\mathbf{B}}\right)^2 \left(\frac{\Delta\tilde{\varepsilon}}{\Delta\tilde{\chi}}\right), \quad U_\mathrm{M} = \frac{\Delta\tilde{\chi}}{2\mu_0}\mathbf{B}^2,$$
$$U_E = \frac{\varepsilon_0 \Delta\tilde{\varepsilon}}{2}\mathbf{E}^2. \quad (5)$$

The parameter ρ is the ratio of the magnetic and electric anisotropic energies, U_M and U_E, respectively. The limiting value of the director orientation depends, therefore, on the material property, $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$, and the known experimental parameters, **E/B** and α. The predicted relationship between the limiting or equilibrium director orientation, θ_∞, and ρ is shown in figure 3 for various values of α. It is clear from the results in this figure that the limiting angle is not exactly the same as the angle between the two fields because the value of ρ is insufficient to align the director parallel to the electric field. What is more apparent is that there is a strong dependence of the variation of θ_∞ with ρ on the angle between the two fields as this tends to 90°. Indeed for this angle the director orientation is predicted to change discontinuously from 0° to 90° when ρ is unity; that is, the two field energies are identical. Given the relationship between the quadrupolar splitting and the director orientation—see equation (1)—then $\Delta\tilde{\nu}$ will also show an analogous variation with ρ, and hence with the applied voltage.

We now turn to the dynamic behaviour of the director; here the relaxation times for the turn-on (τ_ON) and turn-off (τ_OFF) processes are

$$\tau_\mathrm{ON} = \left(\tau_\mathrm{M}^{-2} + 2\tau_\mathrm{M}^{-1}\tau_\mathrm{E}^{-1}\cos 2\alpha + \tau_\mathrm{E}^{-2}\right)^{-\frac{1}{2}} \quad (6)$$

and

$$\tau_\mathrm{OFF}(\equiv \tau_\mathrm{M}) = \gamma_1/(2U_\mathrm{M}) \quad (7)$$

$$\tau_\mathrm{E} = \gamma_1/(2U_\mathrm{E}) \quad (8)$$

where τ_E is the electric field-induced relaxation time for the director.

We can see, therefore, that the static experiments give ρ from which the material property $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ can be determined. The dynamic experiments provide the two pure relaxation times, τ_E and τ_M, for the alignment of the director by electric and magnetic fields, respectively. Since the field strengths are known the relaxation times are related to the material properties $\gamma_1/\Delta\tilde{\varepsilon}$ and $\gamma_1/\Delta\tilde{\chi}$, respectively. The ratio of these is just $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ which permits a check with the static experiments. Both

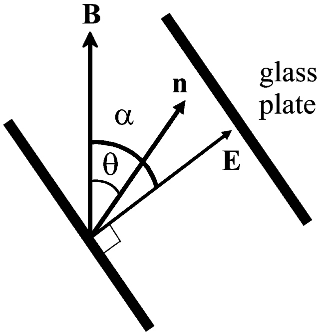

Figure 2. The experimental geometry used in this study. The director, **n**, and electric field, **E**, make the angles θ and α, respectively, with the magnetic field, **B**.

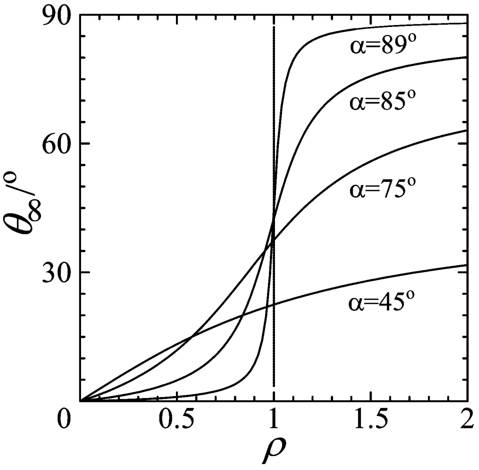

Figure 3. The predicted relationship between the limiting value of the director orientation, θ_∞, and ρ calculated for various values of α. The limiting angle is seen not to be exactly the same as α because the value of ρ is insufficient to align the director parallel to the electric field.

relaxation times, τ_{ON} and τ_{OFF}, are related to the rotational viscosity coefficient but there are advantages to determining τ_{ON} since it is possible to bring this into a measurable range via α and **E**. To obtain the rotational viscosity coefficient it is necessary to know $\Delta\tilde{\chi}$ or $\Delta\tilde{\varepsilon}$ from separate experiments. In practice it proves to be easier to determine accurate values for $\Delta\tilde{\varepsilon}$ than for $\Delta\tilde{\chi}$.

3. Experimental

The nematogen used for our current study is 5CB-d_2, specifically deuteriated in the α-position of the pentyl chain. Thin nematic sandwich cells were prepared from glass plates coated with transparent In_2O_3 to act as electrodes; these were not treated in any way. The cell thickness, *d*, was determined optically and found to be 56.1 μm. The cells were held together by special glue which is stable in the presence of the cyanobiphenyls and which can be cured using UV radiation for a few minutes. The saturation voltage method [24] was employed to measure the surface anchoring strength, $A = 1 \times 10^{-7}\,\mathrm{J\,m^{-2}}$, at the interface of 5CB-d_2 with the substrate surface. This corresponds to a weak anchoring condition and so the surface does not influence the director orientation in the presence of strong electric and magnetic fields. The measurements were made at slightly different temperatures in the nematic phase of 5CB-d_2. The spectra were recorded using a JEOL Lambda 300 spectrometer, which has a magnetic flux density, **B**, of 7.05 T. The spectra measured during the turn-on and the turn-off processes were obtained using quadrupolar echo pulse sequences, with a 90° pulse of 7.7 μs and an interpulse delay of 40 μs; the post delay time was 30 ms [13]. The number of free induction decays used to produce spectra with good signal-to-noise varied from 2 000 to 10 000 depending on the sharpness of the spectral lines. The nematic cell was held in the NMR probe head so that the electric field, whose direction is normal to the substrate surface, makes an angle α with the magnetic field (see figure 2).

Figure 1 shows the spectrum of 5CB-d_2 recorded at 297 K without an electric field; the quadrupolar splitting, $\Delta\tilde{\nu}_0$, is 52.1 kHz. The weak feature in the centre of the spectrum originates from the isotropic phase of 5CB-d_2, possibly dispersed in the glue holding the cell together. The final adjustment of the cell alignment to ensure that the electric field makes the desired angle with the magnetic field was carried out by switching on a high electric field (100 V_{rms}) and rotating the cell by a few degrees, clockwise or counter-clockwise, using the goniometer of the spectrometer, until the appropriate doublet splitting was obtained; see equation (1). However, the electric field will not be at exactly the desired angle because the value of 100 V_{rms} is not quite sufficient to align the director parallel to the electric field [13]. An amplifier and a function generator were used to provide a sinusoidal a.c. electric potential of several kHz to the cell. This frequency is sufficient to overcome the effects of ionic conduction and to provide a time resolution of approximately 0.1 ms during the turn-on and turn-off dynamics measurements. In addition, because this frequency is larger than the inverse of the director relaxation times, the director experiences a constant electric field during the turn-on process, as required in the standard hydrodynamic analysis [25]. On applying or removing the electric field, the monodomain director orientation is expected to move in a plane defined by **B** and **E**.

4. Results and discussion

4.1. *Determination of $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ from the static experiments*

As we have seen in § 2, the angle α between the electric and magnetic fields is one of the important experimental parameters needed to investigate the static and dynamic director orientation. However, it is difficult to determine the angle precisely because the electric field intensity used in our measurements is not quite high enough to align the director parallel to the electric field, as we shall see. After the approximate adjustment of α to the desired value using the goniometer of the spectrometer, its precise value is obtained from the static measurement of the deuterium NMR spectra as a function of voltage. Equations (1) and (4) show that the quadrupolar splitting ratio for a certain applied voltage, V, gives the limiting value of θ_∞. It is of interest, therefore, to rearrange equation (4) combined with equation (1) as

$$g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)=\frac{1}{a\sin 2\alpha}\cdot\frac{1}{V^2}+\cot 2\alpha, \qquad (9)$$

where

$$g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)=\frac{4(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)-1}{2\{[2-2(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)][1+2(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)]\}^{\frac{1}{2}}},$$
$$a=\frac{\mu_0\varepsilon_0}{\mathbf{B}^2d^2}\left(\frac{\Delta\tilde{\varepsilon}}{\Delta\tilde{\chi}}\right). \qquad (10)$$

The function $g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)$ is seen to be linear in $1/V^2$, accordingly α and α, (that is, $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$) can be found from a linear least squares fit of the experimental NMR data to equations (9) and (10).

It is apparent from figure 3 that the condition $\alpha\approx 90°$ will give a critical change of $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$ around the threshold condition of $\rho=1$. Accordingly this should be a good experimental geometry with which to obtain the values of $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ and also α. However, we have also studied the electric field (1 kHz) dependence of the director orientation for three other values of the angle between the magnetic and electric fields. The results of these investigations are shown in figure 4 where the ratio of the quadrupolar splittings, $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$, is used as a measure of the director orientation. In this figure the quadrupolar splitting of 52.1 kHz, for a deuterium spectrum recorded in the absence of an electric field, was used. The experimental results clearly resemble the theoretical predictions shown in figure 3. The optimal values of the ratio $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ and the angle α, were determined by a least squares fit of the data in figure 4 to equations (9) and (10). The values so determined are

$\alpha/°$	89.5	81.3	70.2	58.5
$\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}\times 10^{-6}$	9.03	9.14	9.07	9.12.

These results were used to calculate the voltage dependence of $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$ shown in figure 4 and the predictions are clearly in excellent agreement with experiment. In addition, the ratio $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ is essentially independent of the experimental geometry, as required, being $(9.09\pm 0.04)\times 10^6$. This is in reasonable agreement with the value of $(9.6\pm 0.1)\times 10^6$ previously reported [13], which was obtained by using the data for the director dynamics described in the next section. The ratio $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ has been determined as a function of temperature for 5CB and found to be constant [13]; this results from the fact that both anisotropic susceptibilities, $\Delta\tilde{\varepsilon}$ and $\Delta\tilde{\chi}$, are essentially linear in the second rank orientational order parameter for the molecular long axis [1, 13].

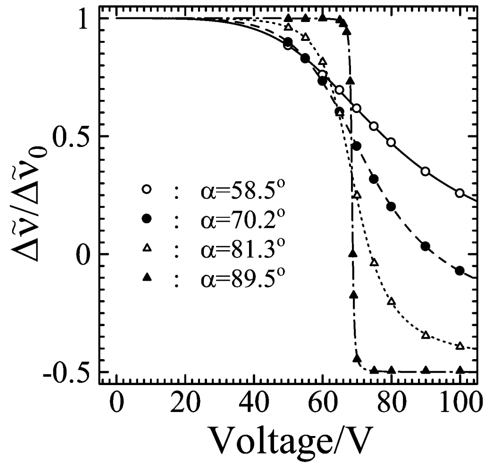

Figure 4. The voltage (1 kHz) dependence of $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$ for 5CB-d_2 at 297 K measured for different experimental geometries with $\alpha=89.5°$ (filled triangles), 81.3° (open triangles), 70.2° (filled circles) and 58.5° (open circles). The quadrupolar splitting, $\Delta\tilde{\nu}_0=52.1$ kHz, for a deuterium NMR spectrum recorded without an electric field, is used to obtain the ratio of the quadrupolar splittings. The solid lines show the least squares fit to equations (1) and (4); this fitting gives the average value for $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ of $(9.09\pm 0.04)\times 10^6$.

4.2. *Determination of the relaxation times from the time-resolved experiments ($\alpha<45°$)*

The nematic cell containing 5CB-d_2 was held in the NMR probe head so that the electric field makes an angle of about 45° with the magnetic field (see figure 2) and the sample temperature was set at 297 K. For the turn-on process the director relaxation was monitored at several values of t_{ON} between 0 and 25 ms following the application of the electric field. For the turn-off process, the director relaxation was measured at several values of t_{OFF} in the range 0 to 25 ms. An electric potential of 50 V was applied for $t_a=50$ ms to obtain the initial director alignment for the turn-off experiments.

Deuterium NMR spectra were obtained during the turn-on and turn-off processes [13]. In the turn-on process, the quadrupolar splitting decreases and then saturates with time, corresponding to the equilibrium alignment of the director. Figure 5 shows the temporal variation in the ratio of the quadrupolar splittings, $\Delta\tilde{\nu}(t)/\Delta\tilde{\nu}_0$, determined from the time-resolved deuterium NMR spectra recorded at 297 K for the turn-on and turn-off processes. We can see that for the turn-on process the director rotates from its initial orientation $\theta_0=0°$ for $\Delta\tilde{\nu}_0=52.1$ kHz, and then aligns at the limiting angle θ_∞ of 29.7° determined from $\Delta\tilde{\nu}_\infty=32.9$ kHz, the limiting value of $\Delta\tilde{\nu}(t)$ as t tends to infinity. In the turn-off process, the time dependence of the director orientation was obtained in the same way and this is also shown in figure 5. The director rotates back to be parallel to the magnetic field and the time taken for the alignment process is longer in the turn-off process than in the turn-on process. From the experimental values of $\Delta\tilde{\nu}_0$ and $\Delta\tilde{\nu}_\infty$ combined with equations (1) and (3), the values of the two relaxation times, τ_{ON} and τ_{OFF}, were obtained by fitting the ratio of the quadrupolar splittings as a function of time for the turn-on and turn-off processes. The solid lines in figure 5 show the best fits, giving the values for τ_{ON} and τ_{OFF} as 0.672 and 1.34 ms, respectively. We have chosen to fit the time dependence of the quadrupolar splitting ratio rather than that for the director orientation calculable from it, because the splitting constitutes the primary experimental data and the absolute error associated with each point is more or less constant. An accurate value for the angle between the magnetic and electric fields of 44.7° was calculated by substituting the value for θ_∞ into equation (4); this angle can also be obtained by using the simpler method described in § 4.1.

In order to calculate the values of $\Delta\tilde{\chi}$ and γ_1 from our results we need the value of $\Delta\tilde{\varepsilon}$ at the same temperature. For this we have used the dielectric anisotropies determined by Dunmur *et al.* [28]. The resultant temperature dependences of $\Delta\tilde{\chi}$ and γ_1 are listed in table II of [13] where $\Delta\tilde{\varepsilon}$ used in the calculation is also given. Here we show that our values of $\Delta\tilde{\chi}$ and γ_1 are in relatively good agreement with those obtained by other studies. We also note that equations (5–8) allow the expression for the turn-on relaxation time to be written as

$$\tau_{\mathrm{ON}} = \frac{\gamma_1}{2U_{\mathrm{M}}}\left(1+2\rho\cos 2\alpha+\rho^2\right)^{-\frac{1}{2}}. \qquad (11)$$

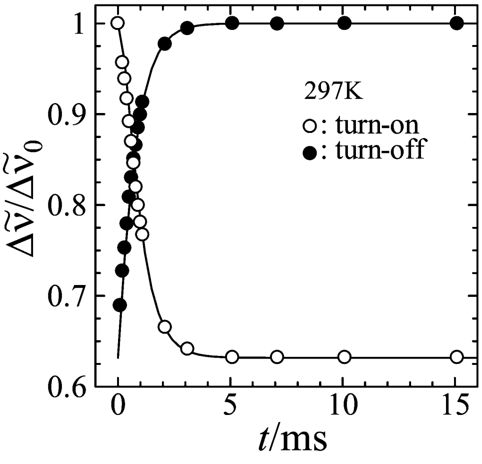

Figure 5. The time dependence of the quadrupolar splitting ratio, $\Delta\tilde{\nu}/\Delta\tilde{\nu}_0$, for the turn-on (open circles) and the turn-off (filled circles) processes determined from the time-resolved deuterium NMR spectra of 5CB-d$_2$ at 297 K; here the experimental value $\Delta\tilde{\nu}_0 = 52.1$ kHz has been used.

It is apparent from this equation that $\Delta\tilde{\chi}$ and γ_1 can be determined by using only one relaxation time, τ_{ON}, and the values of $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ and α, provided of course that $\Delta\tilde{\varepsilon}$ is known from an independent experiment.

4.3. *Field-induced director dynamics for the orthogonal geometry of B and E*

As we have seen, the measurements made when $\alpha<45°$ show that the director is aligned by the relevant field as a monodomain. This leads to the determination of two material properties, namely $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$ and $\gamma_1/\Delta\tilde{\chi}$. However, if the director is not uniform within the sample then it proves possible to determine additional properties of the nematic phase [8]. This intriguing possibility is considered, albeit briefly, in this section. The basic idea to the determination of these properties is to apply the aligning field orthogonal to the initial director orientation. Strictly the aligning torque on the director vanishes for this geometry, and so the director should remain in this metastable state; see equation (2). However, thermal fluctuations in the director orientation induce a change in the torque which grows as the director moves from being orthogonal to the field. More importantly there is a degeneracy in the alignment pathway for the director which may move both clockwise or anticlockwise as it returns to being parallel to the field. As a consequence, a non-uniform director distribution results which allows additional viscosity coefficients as well as the elastic constants to be determined.

Here we describe an example of the application of deuterium NMR spectroscopy to investigate the director dynamics in a nematic liquid crystal subject to orthogonal magnetic and a.c. electric fields. In the absence of the electric field the director for 5CB is aligned parallel to the magnetic field. When the electric field, which is strong enough to overcome the magnetic torque, is applied the director aligns parallel to the electric field. After the electric field is switched off, the director will then align from being parallel to the electric field to being parallel to the magnetic field. In principle it should be possible to monitor the time-dependent changes in the director distribution from the changes in the NMR spectrum during this realignment process.

The time-resolved deuterium NMR spectra recorded during the turn-on process at 293 K are shown in figure 6. The spectra show that the director alignment is complete within 9 ms, by which time the quadrupolar splitting is reduced to half of its initial value; in other words the director is now parallel to the electric field and so orthogonal to the magnetic field. Following the application of the electric field, the director remains parallel to the magnetic field for up to 1.5 ms before starting to change its orientation, i.e. there is an apparent induction period of 1.5 ms for the turn-on process. Then after this induction period, at t=2.5 ms, a second quadrupolar splitting with somewhat broader lines is observed, which corresponds to the director oriented normal to the magnetic field. Furthermore, the spectrum at t=3.5 ms shows that the original lines, associated with θ=0°, have become broader and there is an increase in the spectral intensity in the region between these two lines. This indicates a spread in the director orientation within the extremes of 0° and 90°. Indeed at t=4.5 ms there is an increase in the spectral intensity in the region between the parallel and the perpendicular features of the spectra, showing that the director is increasingly adopting a range of orientations between 0° and 90° to the magnetic field. The form of this powder pattern changes further with time as the director distribution alters to give more of the director normal to the magnetic field. At t=5.5 ms the intensity of the orthogonal features has increased at the expense of the parallel, while at the same time the intensities associated with the splittings originating from intermediate director orientations have increased, showing that the angle between the director and the magnetic field has increased. These processes continue until, after 9 ms, the director is almost uniformly aligned normal to the magnetic field. In summary, the director starts uniformly aligned parallel to the magnetic field then passes through a regime in which its orientational distribution is markedly non-uniform, resulting from the degeneracy in the alignment process, before becoming aligned perpendicular to the magnetic field. During the turn-off process a non-uniform director distribution is also observed during the alignment. Such changes are consistent with those observed for other systems where there is also a degeneracy in the pathways for the director alignment [8].

The alignment process for the change in the director orientation, following the turn-on and turn-off of the electric field orthogonal to the magnetic field, is clearly very complex. The director does not align as a mono-domain and this is perhaps to be expected because of the degeneracy in the alignment pathway. In addition, the alignment process appears to be qualitatively and quantitatively different for the turn-on and turn-off process, possibly because of the difference in the magnitudes of the field torques responsible for the alignment. Analysis of the spectral lineshapes which demonstrate a non-uniform distribution of the director can, in principle, yield not only information about additional viscosity coefficients but also the elastic constants [8]. Our results show that it should be possible to extend the studies of polymeric systems with their high viscosities to nematics of low molecular mass with their significantly lower viscosities and hence relaxation times.

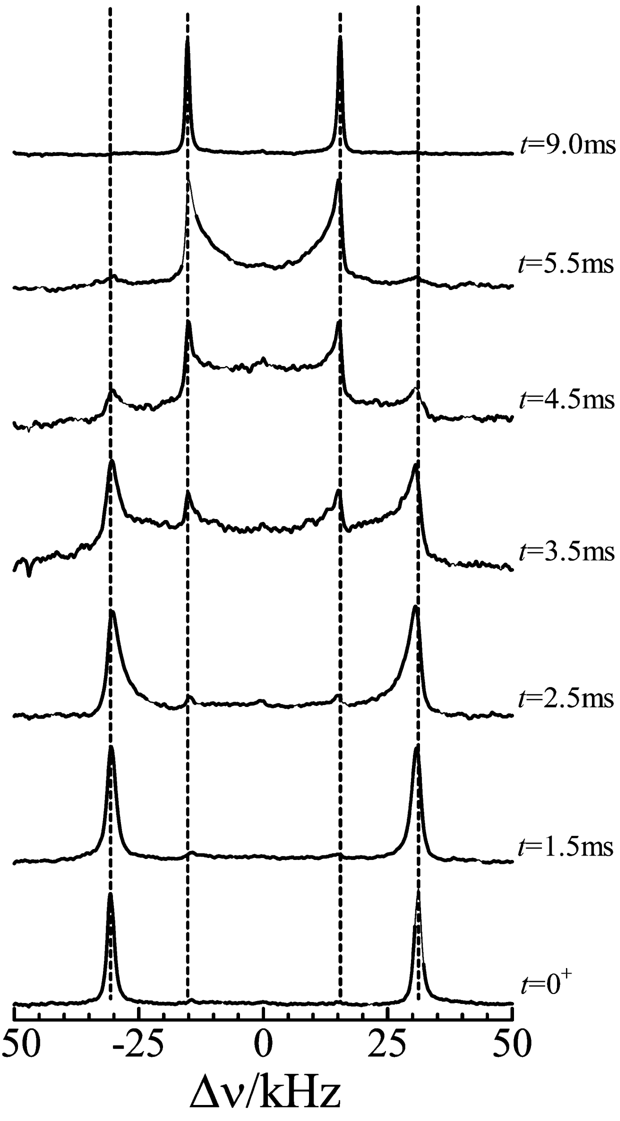

Figure 6. The deuterium NMR spectra of 5CB-d_2 for the turn-on process recorded at 283 K with $\alpha \approx 90°$ after the application of an electric potential (10 kHz, 60 V_{rms}). The time-resolved spectra were measured by changing the duration, t_a, for which the potential was applied.

5. Summary and conclusions

Deuterium NMR spectroscopy has been used to study the equilibrium alignment of the director for a nematic subject to competing electric and magnetic fields. The director orientation was determined as a function of the electric field strength and the angle between the two fields. Analysis of this large data-set based on continuum theory allows the accurate determination of the ratio of the dielectric and diamagnetic anisotropies.

In addition, deuterium NMR spectroscopy was used to investigate the director dynamics in a nematic slab, and time-resolved NMR spectra have been obtained. The nematic cell was held in the NMR probe so that the electric field made an angle of about 45° with the magnetic field. This experimental geometry allowed us to avoid the degeneracy of the realignment pathway for the director found for larger angles. When the electric field was applied to the nematic film, the director moved from being parallel to the magnetic field to being at an angle θ with respect to it. After the electric field was switched off, the director relaxed back to being parallel to the magnetic field. In this way a non-equilibrium director orientation with respect to the field could be created without causing flow to occur within the nematic sample. From the measured relaxation times, we have determined the rotational viscosity coefficient and the diamagnetic anisotropy of 5CB. Both of these quantities were found to be in reasonably good agreement with values reported in the literature. The present results indicate that deuterium NMR spectroscopy provides a valuable technique with which to investigate the director alignment when fields are applied and the times taken to achieve the equilibrium director orientation.

The deuterium NMR technique has also been used to investigate the dynamic director alignment process in a nematic liquid crystal subject to orthogonal magnetic and a.c. electric fields. The time dependence of the NMR spectra shows that the director was rotated from being parallel to the magnetic field to being orthogonal to it when the electric field was switched on. The intermediate states were observed to correspond to a wide director distribution resulting from the degeneracy in the alignment pathways. Although the predicted director dynamics for the orthogonal geometry of **B** and **E** has not been obtained analytically, deuterium NMR spectroscopy clearly provides a very valuable technique with which to investigate the dynamic director distribution. Numerical analysis of such time-resolved NMR spectra should result in the determination of other physical properties of the nematic.

Acknowledgements

This work was supported by a Grant-in-aid for Scientific Research ((B) Project Number: 15360176) from the Japan Society for the Promotion of Science (JSPS), partially supported by MEXT.HAITEKU 2001, and was carried out as an Anglo-Japanese joint research project of the International Exchange program supported by The Royal Society and JSPS.

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