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Dynamics of a Liquid Crystal in its Smectic A Phase from Angle Dependent Deuterium Spin Relaxation Measurements

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Abstract The Zeeman and quadrupolar spin-lattice relaxation times of the aromatic deuterons of OAB-d_{12} were measured throughout the smectic A phase at two different frequencies (15 and 46.04 MHz). At 15 MHz measurements were performed as a function of the angle between the phase director and the external magnetic field. Eight spectral densities were consequently determined, and were analyzed by means of a global target fitting procedure using diffusional models for the overall molecular reorientations and the internal motions. Diffusional coefficients of about 10^9 s^{-1} were found for molecular spinning and phenyl ring rotations, three orders of magnitude higher than for molecular tumbling.

Keywords: deuterated smectic liquid crystals; ^2H NMR; orientation dependent quadrupolar and Zeeman spin-lattice relaxation times; diffusional coefficients; molecular dynamics.

INTRODUCTION

Deuterium spin relaxation measurements are commonly acknowledged as a useful means to study molecular dynamics in liquid crystals. In fact, deuterium relaxation processes are governed by the quadrupolar interaction and can therefore be interpreted avoiding the complications arising from intra- and intermolecular dipolar interactions. Moreover, the possibility of using selective labelling allows one to get more detailed information on the overall molecular motions as well as to investigate the internal motions of different molecular fragments.

In liquid crystalline systems the dynamic processes contributing to deuterium relaxation are molecular reorientations and segmental motions, as well as low frequency collective motions such as the characteristic fluctuations of the phase director orientation.

A suitable choice of relaxation experiments permits to determine individual spectral densities of motion, which characterize the spectrum of molecular fluctuations, as a function of the temperature. In numerous studies deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times have been used to determine $J_1(\omega_0)$ and $J_2(2\omega_0)$ at different temperatures which have been interpreted within diffusional models in order to account for the contributions of different types of motion to the deuterium spin relaxation rates[1].

Since the spectral density describes the frequency distribution of the various modes of molecular motions, it would be important, however, to carry out relaxation experiments at different field strengths in order to determine the individual spectral densities also as a function of frequency. Studies of this type are usually performed by field cycling techniques which allow the contribution of slow motions, as the order director fluctuations, to be investigated. These measurements are however limited in the kHz frequency range up to a few MHz[2]. Above this range, the frequency dependence of the individual spectral densities

J_1 and J_2 has been investigated in few cases since for studies of this type the availability of spectrometers working at different magnetic fields is required. The problem may be partly overcome by exploiting the orientational dependence of the spectral densities in anisotropic samples, which can be investigated through the angular dependence of the relaxation rates. In fact the measurement of T_{1Z} and T_{1Q} as a function of the angle between the director of the mesophase and the external magnetic field allows the spectral densities J_0, J_1 and J_2 at two different frequencies (ω_0 and $2\omega_0$) to be determined. Angular dependent Jeener-Broekaert experiments, yielding T_{1Z} and T_{1Q} simultaneously, thus represent a convenient way of accessing spectral densities which otherwise would require instrumentation at different field strengths. Experiments of this type have been performed in very few cases and only in fairly viscous smectic phases, which do not reorient back to the magnetic field after rotation[3], or in macroscopically oriented lipid bilayers[4].

In the present work the dynamics of a partially deuterated mesogen (4,4'-di-*n*-octylazoxybenzene, OAB) in its smectic A phase is investigated. In previous papers a detailed analysis of the deuterium spectrum of OAB-d_{12}, as well as an investigation of its structural and ordering properties were performed[5] and the dynamic behaviour was preliminarily studied measuring T_{1Z} at a single frequency[6]. Here an investigation of the angular dependence of the Zeeman and quadrupolar spin-lattice relaxation times is presented. T_{1Z} and T_{1Q} were determined simultaneously by the Jeener–Broekaert pulse sequence at six different orientations of the sample with the external magnetic field. The realignment of the sample after rotation was avoided using a spectrometer working at low magnetic field. Measurements of T_{1Z} and T_{1Q} were also performed at a different Larmor frequency with the phase director aligned with the external magnetic field. The study was preliminarily limited to the aromatic deuterons.

THEORY

Quadrupolar (T_{1Q}) and Zeeman (T_{1Z}) spin-lattice relaxation times are related to the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ through the following relationships:

$$\frac{1}{T_{1Z}}(\Omega) = J_1(\omega_0,\Omega) + 4J_2(2\omega_0,\Omega) \quad (1)$$

$$\frac{1}{T_{1Q}}(\Omega) = 3J_1(\omega_0,\Omega) \quad (2)$$

where $\Omega = (\theta,\phi)$ denotes the polar angles of the phase director in the laboratory frame defined by the external magnetic field and ω_0 is the Larmor frequency.

Since theoretical models[1] have been proposed which interpret the spectral densities at $\theta = 0$ (which for simplicity we will refer to as $J_{m_L}(\omega)$, without explicitly indicating the angle) in terms of dynamic parameters of individual motions occurring in liquid crystalline phases, it is useful to write the relationships linking the angle dependent spectral densities to $J_{m_L}(\omega)$. In a general case these expressions are quite complicated[7], but they simplify when a well defined symmetry of the phase is taken into account. In particular, for uniaxial liquid crystalline phases, where the ϕ dependence disappears, the following relationships hold[3]:

$$J_1(\omega,\theta) = \frac{3\cos^2\theta\sin^2\theta}{2}J_0(\omega) + \frac{1-3\cos^2\theta+4\cos^4\theta}{2}J_1(\omega) + \frac{1-\cos^4\theta}{2}J_2(\omega) \quad (3)$$

$$J_2(\omega,\theta)=\frac{3(1-\cos^2\theta)^2}{8}J_0(\omega)+\frac{1-\cos^4\theta}{2}J_1(\omega)+\frac{1+6\cos^2\theta+\cos^4\theta}{8}J_2(\omega) \quad (4)$$

It is evident from equations (1)-(4) that, whereas standard measurements at $\theta = 0$ allow one to obtain only the two spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$, four more spectral densities, namely $J_0(\omega_0)$, $J_0(2\omega_0)$, $J_1(2\omega_0)$ and $J_2(\omega_0)$, become available when measurements are performed at several θ angles. Moreover, the experimental data set can be further enriched by extending the measurements at different Larmor frequencies.

Spectral densities contain all the dynamic information, but in a quite implicit form. Therefore it would be useful to express them in terms of other quantities which can discriminate the contributions to the relaxation arising from the different motional processes. In fact, the complex dynamics of liquid crystals is characterized by the combined effect of three types of motions: overall reorientations of the whole molecule, internal rotations or jumps of molecular fragments and collective motions.

The autocorrelation functions $g_{m_L m_M}(t)$ relative to the overall molecular motions can be expressed, following Vold and Vold[8], as a sum of decreasing exponential functions:

$$g_{m_L m_M}(t)=c_{m_L m_M}\sum_j a^{(j)}_{m_L m_M}\exp\left(-\frac{t}{\tau^{(j)}_{m_L m_M}}\right) \quad (5)$$

The corresponding spectral densities $J_{m_L m_M}$ can thus be obtained as the Fourier transforms of such autocorrelation functions and are then combined in an expression giving the experimental quantities J_{m_L}.

In the present work overall molecular reorientations are treated within the model of Nordio *et al.*[9], while the internal motions are

considered superimposed and assumed to obey the strong collision model[10]. In this context, the following expression for the spectral densities of the aromatic deuterons is obtained:

$$J_{m_L}(\omega) = \frac{3\pi^2}{2}(\nu_q)^2 \sum_{m_M=-2}^{2} \sum_{m_R=-2}^{2} c_{m_L m_M} \left[d^2_{m_R 0}(\beta_{i,Q_i})\right]^2 \left[d^2_{m_M m_R}(\beta_{M,i})\right]^2 \sum_j a^{(j)}_{m_L m_M} \frac{(\tau^{(j)}_{m_L m_M})^{-1} + (1-\delta_{m_R})D_R}{\omega^2 + \left[(\tau^{(j)}_{m_L m_M})^{-1} + (1-\delta_{m_R})D_R\right]^2} \tag{6}$$

where ν_q is the quadrupolar coupling constant; $d^2_{rs}(\beta)$ are the reduced Wigner matrices; β_{i,Q_i} is the angle between the C-D bond and the ring *para* axis; $\beta_{M,i}$ is the angle between the ring *para* axis and the molecular long axis; D_R is the diffusion coefficient relative to the ring rotation about its *para* axis; $a^{(j)}_{m_L m_M}$ represent normalized relative weights of each exponential function with time constant $\tau^{(j)}_{m_L m_M}$; $c_{m_L m_M}$ are the initial amplitudes of the correlation functions. The correlation times $\tau^{(j)}_{m_L m_M}$ are expressed in terms of diffusional coefficients for the overall molecular motions[1]:

$$\frac{1}{\tau^{(j)}_{m_L m_M}} = \frac{6D_\perp}{b^{(j)}_{m_L m_M}} + m_M^2 (D_{//} - D_\perp) \tag{7}$$

where $D_{//}$ and $D_\perp$ are the principal components of the diffusion tensor, diagonalized in a molecular frame, describing the molecular spinning and tumbling motions, respectively.

The coefficients $a^{(j)}_{m_L m_M}$, $b^{(j)}_{m_L m_M}$ and $c_{m_L m_M}$ of equation (6) and (7) have been calculated in reference 8 as a function of the principal order parameter S_{ZZ} for a Maier-Saupe potential.

Theories exist for nematic and low-order smectic phases[11] which describe the contribution to the spectral densities of order director

fluctuations, considered uncoupled to reorientational motions. Such contribution is predicted to be null for $J_0(\omega)$ and $J_2(\omega)$, and to show a typical $\omega^{-1/2}$ frequency dependence for $J_1(\omega)$[12]:

$$J_1^{DF}(\omega) = \frac{3\pi^2}{2}(\nu_q)^2\left[d_{00}^2(\beta_{i,Q_i})\right]^2\left[d_{00}^2(\beta_{M,i})\right]^2(S_{ZZ})^2 T\frac{a_{DF}}{\sqrt{\omega}} \qquad (8)$$

where the factor a_{DF} depends on macroscopic parameters such as the average Frank elastic constant, the viscosity coefficient and the autodiffusion translational constant.

Equations (6) - (8) can be used to interpret the spectral densities, calculated from the experimental relaxation times following equations (1) - (4), in terms of diffusional coefficients relative to the different motional processes.

EXPERIMENTAL

The sample 4,4'-di-*n*-octylazoxybenzene (OAB-d_{12}), completely deuterated at the aromatic sites and at the methylene units closest to the two aromatic rings, was available from a previous study[5]. OAB shows a smectic A phase between 311.8 and 337.4 K and a short nematic range (337.4 – 339.6 K).

^{2}H NMR experiments were performed on a Varian VXR-300 spectrometer working at 46.04 MHz and on a Varian XL-100 spectrometer, working at variable frequency, interfaced with a Stelar DS-NMR acquisition system. The temperature control was good to 0.1 degree on both spectrometers. ^{2}H spin-lattice Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times were measured by means of the broadband Jeener-Broekaert pulse sequence (90_0-$2\tau_1$-67.5_{270}-$2\tau_1$-45_{90}-τ_1-45_{90}-τ_2-45_0)[13]. Relaxation measurements with the phase director aligned parallel to the external magnetic field were performed on the

Varian VXR-300 spectrometer every 2 degrees, on cooling from the isotropic phase, in the temperature range 311 – 333 K. The 90-degree pulse was 22 μs; the Jeener-Broekaert experiments were performed using $\tau_1 = 9$ μs, experimentally optimized, τ_2 ranging from 50 μs to 150 ms and a relaxation delay of 150 ms. In these experiments 128 scans were sufficient to obtain a good signal-to-noise ratio.

Relaxation measurements were performed, on the Varian XL-100 Stelar-interfaced spectrometer, at 15 MHz, at angles of 0, 20, 30, 40, 75 and 90° between the phase director and the external magnetic field and every 4 degrees on cooling from the isotropic phase, in the temperature range 311 – 335 K. The angle was set by means of a goniometer placed over the sample tube. The 90-degree pulse was 8.2 μs; the Jeener-Broekaert experiments were performed using $\tau_1 = 28$ μs, experimentally optimized, τ_2 ranging from 20 μs to 150 ms, a relaxation delay of 150 ms and 1024 scans.

In a Jeener-Broekaert experiment the sum (M_+) and difference (M_-) of the integrals of the two components of a quadrupolar doublet, reported as a function of τ_2, give T_{1Z} and T_{1Q}, respectively, through the two fitting equations:

$$M_+(\tau_2) = a\left[1 - b\exp\left(-\frac{\tau_2}{T_{1Z}}\right)\right] \tag{9}$$

$$M_-(\tau_2) = c + d\exp\left(-\frac{\tau_2}{T_{1Q}}\right) \tag{10}$$

which slightly differ from those theoretically predicted[14] taking account of both incomplete inversion at vanishing variable delays and small spectral asymmetries[15].

In the variable angle measurements, the spectral densities $J_0(\omega_0)$, $J_0(2\omega_0)$, $J_1(\omega_0)$, $J_1(2\omega_0)$, $J_2(\omega_0)$ and $J_2(2\omega_0)$ were obtained at each temperature from the experimental spectral densities by means of a fitting procedure using equations (3) and (4).

Diffusional coefficients were obtained as described in the theory section, using the CAGE software[16] and the geometric, magnetic and order parameters previously reported[5], with the long molecular axis parallel to the *para* axis of the more oriented aromatic ring. However, since the non equivalent aromatic deuterons could not be distinguished in all the spectra, in the dynamic analysis it was necessary to assume the two rings equivalent using average geometric parameters and the same D_R.

RESULTS AND DISCUSSION

An example of the aromatic region of the ^{2}H-NMR spectra of OAB recorded at different orientations are shown in figure 1.

The spectra can be considered, to a first approximation, as consisting of two doublets, the external one arising from the aliphatic deuterons and the internal one from the aromatic ones. At orientations far from the magic angle, the latter doublet shows a fine structure due to the inequivalence of the aromatic rings, their *para* axes making an angle of 16.6°, and there being small differences in the angles between the C-D bonds and the phenyl axes[5].

The differences in the spectra observed at the different tilt angles follow the expected behaviour, i.e. the orientational dependent spectral features, such as the quadrupolar splittings, vary by a factor of $(3\cos^2\theta - 1)/2$ when the phase director is tilted from the magnetic field direction by an angle θ. It is important to note that the correspondence between the tilt angle set by the user and the angle between the phase director and the external magnetic field remained even after several

hours, allowing relaxation experiments to be performed. This might

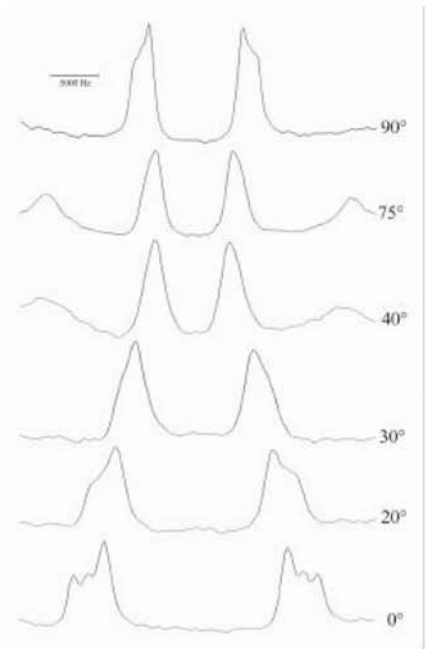

FIGURE 1 Aromatic region of the ^{2}H-NMR spectra of OAB-d_{12} recorded at 319 K and at different angles between the phase director and the external magnetic field. The external doublet appearing at 40° and 75° is due to the aliphatic deuterons.

seem somewhat surprising considering that we are dealing with a low order smectic phase; however, the magnetic field used is sufficiently low to prevent the realignment of the sample. The strong superposition of the aromatic peaks at certain tilt angles did not allow individual relaxation times for the inequivalent aromatic deuterons to be determined. Therefore a single T_{1Z} and T_{1Q} from each Jeener-Broekaert experiment was obtained for all the aromatic deuterons. These values were used to

determine angle dependent spectral densities according to equations (1) and (2). The angle dependent J_1's and J_2's allowed the spectral densities J_0, J_1 and J_2 at ω_0 and $2\omega_0$, with $\omega_0/2\pi$ = 15 MHz, to be obtained in a fitting procedure using equations (3) and (4). As an example, figure 2 shows the experimental values of $J_1(\omega_0,\theta)$ and $J_2(2\omega_0,\theta)$ with the corresponding fitting curves at 335 K.

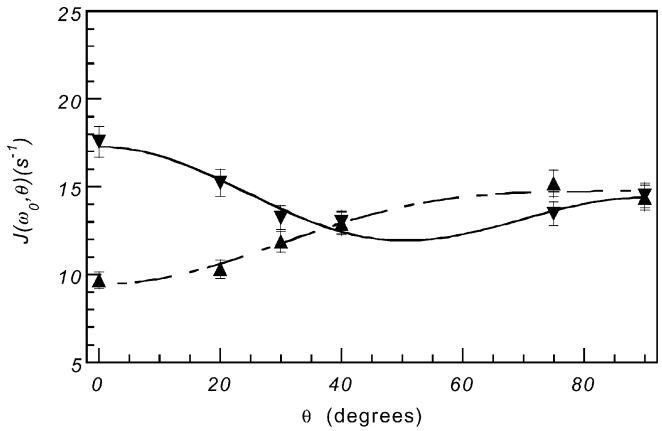

FIGURE 2 Experimental $J_1(\omega_0,\theta)$ (▼) and $J_2(2\omega_0,\theta)$ (▲) at $\omega_0/2\pi$ = 15 MHz and T = 335 K as a function of θ, and corresponding fitting curves.

Measurements of T_{1Z} and T_{1Q} were also performed at a Larmor frequency of 46.04 MHz with the phase director aligned along the magnetic field thus obtaining J_1 and J_2 at yet another frequency.

All the spectral densities $J_{m_L}(\omega)$ determined are reported in figure 3 as a function of the temperature. It must be noticed that the different spectral densities are characterized by quite different errors. This is to be expected considering the different angular coefficients in equations (3) and (4). In particular, given the set of θ values used in the present work, a propagation of errors yields the following relationships: $\sigma(J_0) > \sigma(J_2) > \sigma(J_1)$ at ω_0 and $\sigma(J_0) > \sigma(J_1) > \sigma(J_2)$ at $2\omega_0$.

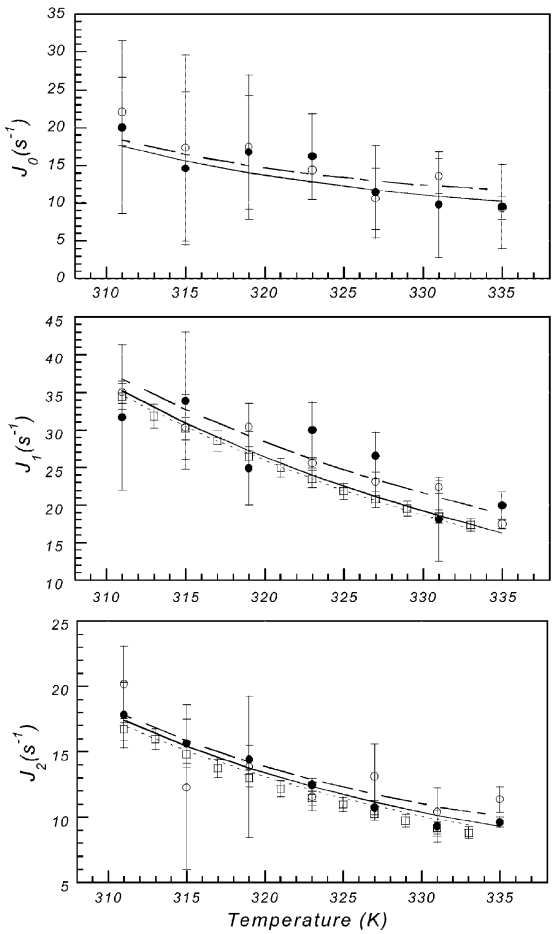

FIGURE 3 Experimental spectral densities and corresponding fitting curves: J_{m_L}(15 MHz) (○ and dashed lines), J_{m_L}(30 MHZ) (● and solid lines), J_1(46.04 MHZ) and J_2(92.08 MHZ) (□ and dotted lines).

All the spectral densities show a decreasing trend with increasing temperature, indicating that at least the motions mostly contributing to

the relaxation are in a fast motion regime. Moreover, they do not show evidence of a strong frequency dependence.

The experimental spectral densities were analyzed within the model of Nordio *et al.* for the overall molecular motions, superimposed to the strong collision model for the internal rotation of the phenyl rings about their *para* axes. To this end a global target fitting procedure was used (see equations (6) and (7)), where an Arrhenius-type temperature dependence of the diffusional coefficients was assumed and the order director fluctuations contribution to the relaxation was neglected. The fitting curves are shown in figure 3 and the optimized diffusional coefficients are reported in figure 4 as a function of the temperature.

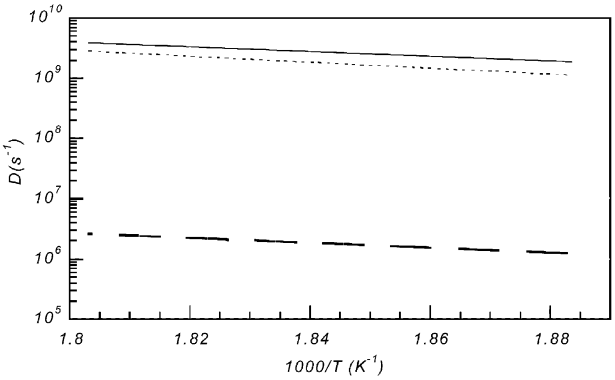

FIGURE 4 $D_{//}$ (solid line), $D_{\perp}$ (dashed line) and D_R (dotted line) as a function of 1000/T.

The resulting $D_{//}$ and D_R are of the same order of magnitude (10^9 s^{-1}), whereas $D_{\perp}$ is about three orders of magnitude smaller, as normally found in smectic phases. The activation energies of the three motional processes are similar, being 23.9, 25.0 and 30.8 kJ/mol for the spinning, tumbling and internal ring motion, respectively, in good agreement with previous findings[6]. It must be noticed that the use of the whole set of experimental spectral densities allows a reliable

determination of $D_{\perp}$, while this diffusion coefficient remained substantially indetermined in a fitting procedure performed using only $J_1(\omega_0)$ and $J_2(2\omega_0)$ at a single Larmor frequency. Attempts to fit the data also including the order director fluctuations contribution did not yield good results, as expected on the basis of equation (8), where the term $d^2_{00}(\beta_{i,Q_i}) = (3\cos^2\beta_{i,Q_i} - 1)/2$ almost vanishes for aromatic deuterons. The small frequency dependence highlighted in the fitting curves is therefore not ascribable to order director fluctuations, but rather to the tumbling motion which, resulting to be in the intermediate regime, gives $(\tau^{(j)}_{m_L 0})^{-1}$ values comparable to ω (see equations (6) and (7)).

CONCLUSIONS

In this study the Zeeman and quadrupolar spin-lattice relaxation times of the aromatic deuterons of OAB-d_{12} were measured at 15 and 46.04 MHz as a function of the temperature. At the lower field the absence of realignment of the phase director following tilting from the external magnetic field direction allowed angle dependent relaxation measurements to be performed, thus giving access to a considerably larger number of spectral densities. The availability of a set of spectral densities at different frequencies throughout the smectic A phase revealed to be useful in order to remove uncertainties in the results obtained from the analysis of the experimental data in terms of diffusional models. Diffusional coefficients of the order of 10^9 s^{-1} were obtained for molecular spinning and internal phenyl ring rotations, and of 10^6 s^{-1} for molecular tumbling. A more complete characterization of the molecular dynamics of this smectogen would require the investigation of the order director fluctuations. To this end similar measurements of T_{1Z} and T_{1Q} of the methylene deuterons of OAB-d_{12}, which, given the larger

quadrupolar splittings, have more stringent experimental requirements, will be performed.

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