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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Eastman, M. P. , Freiha, B. A. , Kessel, B. and Chang, C. Allen(1986) 'Magnetohydrodynamics Of Nematic Mesophases by E.S.R.', *Liquid Crystals*, 1: 2, 147 – 153

To link to this Article: DOI: 10.1080/02678298608086501

URL: <http://dx.doi.org/10.1080/02678298608086501>

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Magneto hydrodynamics of nematic mesophases by E.S.R.

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(Received 28 October 1985; accepted 15 January 1986)

The transient behaviour of the director of a nematic mesophase subjected to spinning at frequency Ω in an applied magnetic field H_0 is investigated by E.S.R. All experiments were conducted with $\Omega > \Omega_c$, $\Omega_c = (\Delta\chi H_0^2/2\lambda_1)$. Here $\Delta\chi$ is the anisotropic magnetic susceptibility and λ_1 is the rotational twist viscosity of the nematic. The theory of Leslie, Luckhurst and Smith is used to analyse Fourier transformed time domain data and their result for the dependence of ω , the director rotation rate, on Ω ($\omega = (\Omega^2 - \Omega_c^2)^{1/2}$) is confirmed for a range of values of H_0 and Ω . Values of Ω_c for Phase IV, Phase V and the alkylcyanobiphenyls K15, K18 and K21 are reported. Linewidths in the frequency domain are shown to depend on the twist viscosity of the mesophase and possible evidence for microdomains in Phase IV and Phase V is presented. The values of Ω_c reported for Phase IV differ by a constant from the values calculated using literature values of λ_1 and $\Delta\chi$.

1. Introduction

Leslie, Luckhurst and Smith (LLS) applied continuum theory to the problem of a nematic liquid crystal spinning at frequency Ω in a static magnetic field H_0 [1]. They defined a critical rotation frequency Ω_c , where

$$\Omega_c = \frac{\Delta\chi H_0^2}{2\lambda_1}. \quad (1)$$

Here λ_1 is the twist viscosity for the nematic phase and $\Delta\chi$ is the anisotropy in the diamagnetic susceptibility. LLS predicted that when Ω is greater than Ω_c the rotation frequency of the nematic phase director, ω , will be given by

$$\omega = (\Omega^2 - \Omega_c^2)^{1/2}. \quad (2)$$

As a test of equation (2) LLS used E.S.R. spectroscopy to investigate a rotating sample of nematic Phase IV doped with 2,2,6,6-tetramethylpiperidine deconat-4, oxyl-I. Their experiment consisted of observing the transient behaviour of one point on a hyperfine line as the sample was spun under the conditions $\Omega > \Omega_c$. LLS published an interesting time domain spectrum and briefly discussed the Fourier transform of that spectrum.

This paper reports the first detailed E.S.R. investigation of the behaviour of ω for $\Omega > \Omega_c$ and shows for the first time that useful information may be obtained from linewidths in the frequency domain. A comparison of experimental values of Ω_c for Phase IV, determined from (2), with values calculated using (1), where $\Delta\chi$ and λ_1 are obtained from the literature, is presented for an extended temperature range. Experimental results for a series of cyanobiphenyls are used to show that even-odd effects are reflected in Ω_c and the field dependence of Ω_c is verified experimentally.

2. Experimental

The nematic liquid crystals Phase IV, Phase V, 4-cyano-4'-n-pentyl biphenyl (K15), 4-cyano-4'-n-hexyl biphenyl (K18) and 4-cyano-4'-n-heptyl biphenyl (K21) were obtained from EM Laboratories, Inc. Di-tert-butyl-nitroxide (DTBN) was obtained from Eastman Organic Chemicals and vanadyl acetylacetonate (VOAcAc) from Alpha Products. The DTBN was used as received while the VOAcAc was purified by recrystallization from acetone. The samples were prepared in thin walled 3 mm i.d. quartz tubes and were degassed on a vacuum line. It has been reported in the literature, and we have confirmed, that wall effects do not appear to be significant for spinning experiments involving sample tubes having an i.d. greater than 1 mm [2].

The E.S.R. spectrometer used in this work has been described elsewhere [3]. In the experiments reported here 100 kHz field modulation was used and the response time of the V-4560 modulation unit was set at 0.001 s. Modulation amplitudes were less than 10 per cent and usually less than 5 per cent of the measured linewidth. The temperature of the sample was controlled by means of a Varian E-257 variable temperature unit.

In a typical experiment H_0 was set at the maximum of a hyperfine line in the first derivative E.S.R. spectrum of the probe and the sample was rotated using a commercial 15 V d.c. motor controlled by a variable d.c. power supply. The time between the start of spinning and the attainment of the spinning frequency Ω was less than Ω^{-1} . The resulting time domain signal was fed to a Hewlett-Packard HP-87XM computer through a HP-3437A digital voltmeter. Typically 256 or 512 points were taken over a time interval of 0.5 to 1 min. Frequency domain spectra were produced by Fourier transforming the time domain signal using the Hewlett-Packard series 80 waveform analysis pack. Microphonic noise was minimized by firmly anchoring the top of the variable temperature dewar using a special collet and by stabilizing the motion of the sample in the dewar using the spinner unit from a Varian A-60 N.M.R. The spinner unit was mounted on the collet directly above the dewar.

3. Experimental results

Figure 1 present the time domain spectrum for DTBN in nematic K15 at 302 K. This spectrum shows a periodic signal at $\sim 2\Omega$ ($\Omega = 0.4$ Hz) having an amplitude which decays with time to a nearly constant value. For the nematic phase the rate of decay is found to increase with temperature. When the sample is isotropic the time domain signal is constant with time and of much smaller amplitude. The information contained in a time domain spectrum like figure 1 is more clearly seen after transformation of the spectrum to the frequency domain.

Figure 2 shows a portion of the frequency domain signal for the DTBN in K15 at four temperatures within the nematic range of K15. These frequency spectra show three lines; a temperature independent line at the spinning frequency (0.3 Hz), a temperature independent harmonic at twice the spinning frequency and a line which occurs at decreasing frequency as the temperature increases. The temperature dependent line disappears when the sample becomes isotropic and thus, is assigned to the rotation of the director in the nematic sample. Because the E.S.R. spectrum of the probe molecule is at a maximum for rotation angles of 0° and 180° the temperature dependent line occurs at 2ω in the frequency spectrum.

Equation (2) predicts that ω^2 has a linear dependence on Ω^2 . This prediction is confirmed experimentally. For example, for Phase IV at 308 K a plot of ω^2 versus

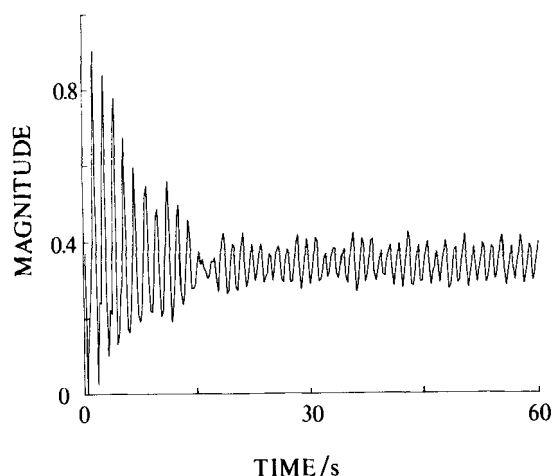


Figure 1. Time domain spectrum for 7×10^{-3} M DTBN in K15; $T = 302.5$ K, $\Omega = 0.4$ Hz, $H_0 = 3317$ G.

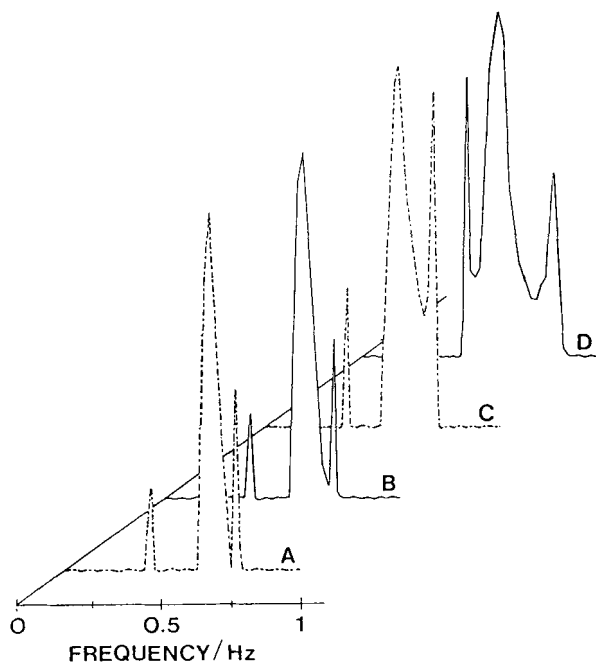


Figure 2. Frequency domain spectrum for 7×10^{-3} M DTBN in K15 at (A) 300.5 K, (B) 301.5 K, (C) 302.5 K, and (D) 303.5 K; $\Omega = 0.3$ Hz and $H_0 = 3317$ G.

Ω^2 ($0.3 \text{ Hz} < \Omega < 1.4 \text{ Hz}$) is linear with a slope of 0.98 ± 0.04 and an intercept of -0.03 ± 0.01 Hz. Except as noted the values of Ω_c reported are determined from the intercepts of plots of ω^2 versus Ω^2 . LLS indicated their experimental data generally supported a linear dependence of ω^2 on Ω^2 but no actual data were presented.

Figure 3 shows the value of Ω_c for Phase IV as a function of temperature. This figure gives 0.32 Hz as the value of Ω_c for Phase IV at 322 K; experiments of a substantially different nature, carried out by Luckhurst *et al.*, for the case $\Omega < \Omega_c$

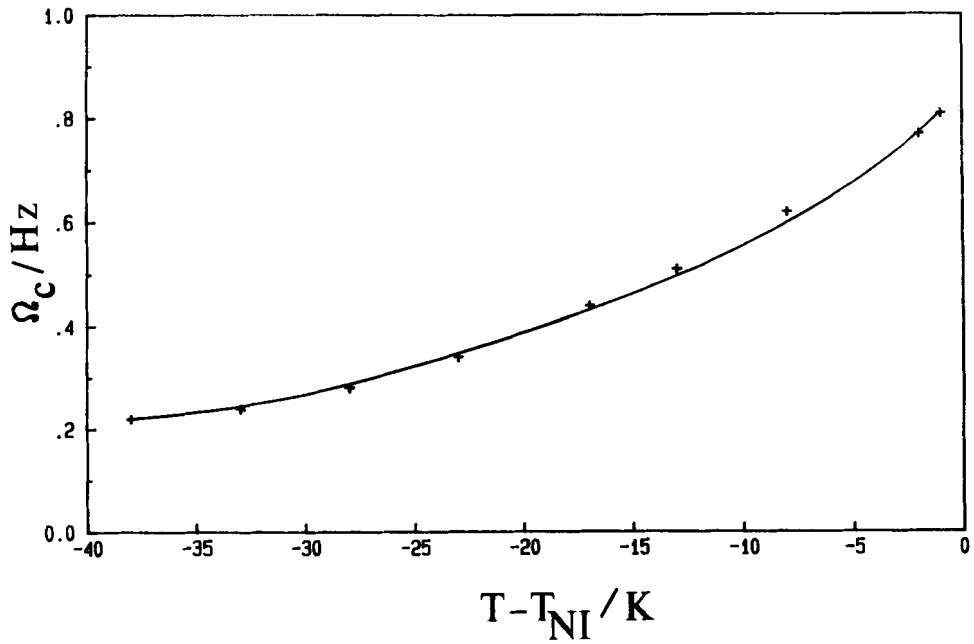


Figure 3. Ω_c versus temperature for 7×10^{-3} DTBN in Phase IV, $H_0 = 3316 \text{ G}$ and $T_{NI} = 344 \text{ K}$.

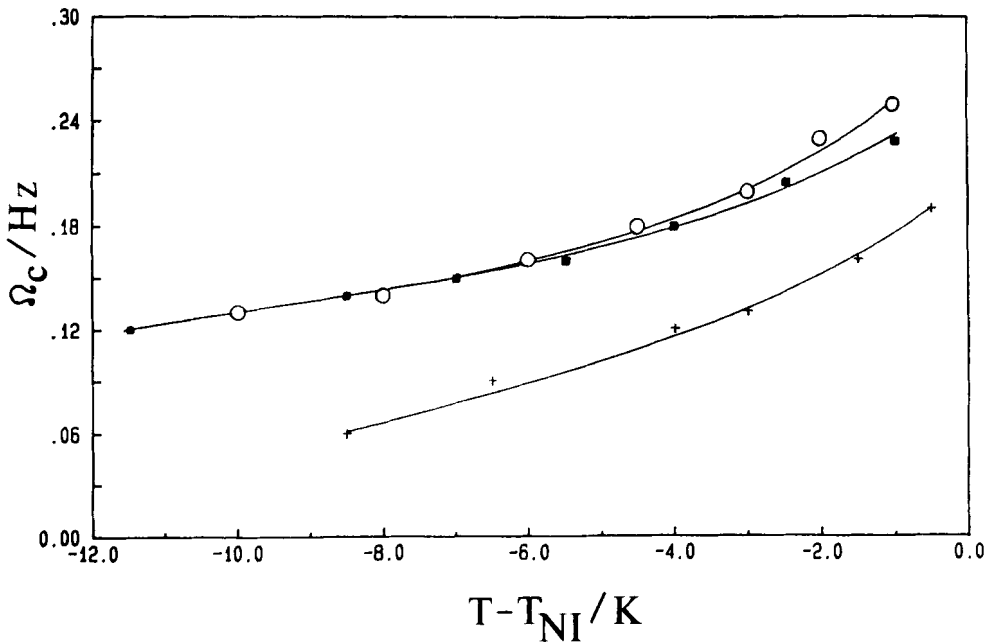


Figure 4. Ω_c versus temperature for 7×10^{-3} DTBN in K15 ($T_{NI} = 306 \text{ K}$) (\circ), K18 ($T_{NI} = 301 \text{ K}$) (+) and K21 ($T_{NI} = 314 \text{ K}$) (\blacksquare); $H_0 = 3317 \text{ G}$.

yielded a value of 0.28 Hz for Ω_c at 322 K [2]. Figure 4 shows the values of Ω_c determined for K15, K18, K21 as a function of T_r . Here $T_r = (T - T_{NI})/T_{NI}$ and T_{NI} is the clearing temperature. It is clear from this figure that K15 and K21, have substantially larger values of Ω_c than K18. This is a reflection of the even-odd effect noted for the transition temperatures and order parameters of the alkylcyano-biphenyls [4]. In general, the transition temperatures and the order parameters for the alkylcyanobiphenyls with an odd number of carbon atoms in the alkyl side chain are larger than those having an even number. Since the order parameter is related to the anisotropy in the magnetic susceptibility, one might expect, based on the contribution of $\Delta\chi$ to Ω_c , that the values of Ω_c for the odd members of the series would be larger than those for the even members [5]. In addition, the values of λ_1 for K18 and K21 are smaller than for K15; thus, λ_1 contributes to the effect seen in figure 4 [6]. It is interesting to note that when Ω_c for K15, K18 and K21 are plotted versus reduced temperature, the data for K15 and K21 lie virtually on the same line.

The line in the frequency spectrum due to the rotation of the director has a width with the potential to provide useful information. This width reflects the rate of decay of the amplitude of the time domain signal in figure 1 and is related to the time required for the director to seek a new distribution in the spinning sample. Aspects of this process have been discussed by Luckhurst and co-workers [2]. Because the linewidth increases as the spinning rate decreases; it seems reasonable to relate the linewidth at a given Ω and T to the inverse of the twist viscosity of the nematic at T . A plot of linewidth (at half height $\Omega = 1.3$ Hz) for DTBN in Phase IV versus the inverse of the literature values for the twist viscosity is linear over the temperature range 308 K to 333 K [7]. The correlation coefficient for this plot is 0.98. A similar plot for DTBN in K15 over the much narrower temperature range 299 K to 305 K has a correlation coefficient of 0.99.

The field dependence of Ω_c can be verified using a paramagnetic probe which has a large hyperfine splitting and measuring the value of Ω_c for each of the hyperfine lines in the spectrum. For example, the eight hyperfine lines in the X-band spectrum of VOAcAc in Phase V are separated by ~ 81 G; thus experiments can be carried out over a reasonable range of magnetic field values. A plot of Ω_c determined for each of the hyperfine lines in the spectrum of VOAcAc in Phase V at 318 K, versus H_0^2 is linear with a least squares slope of $(3.7 \pm 0.4) \times 10^{-9}$ Hz/G² and an intercept of -0.08 ± 0.04 Hz. The value of Ω_c/H_0^2 determined from the slope agrees within experimental error with the value of Ω_c/H_0^2 determined for DTBN in Phase V (3.3×10^{-9} Hz/G²). This result indicates that the techniques described here are, within experimental error, probe independent. Similar conclusions, concerning probe independence, were reached in an E.S.R. study of the transient response of a nematic to a redirected magnetic field [8]. DTBN, though weakly ordered in nematic phases, was chosen for the majority of experiments reported here since experiments at the beginning of our work showed the values of ω measured using more anisotropic nitroxide probes did not differ for those determined using DTBN. It should be noted that the solubility of VOAcAc in nematic phases is often low and as a consequence the signal to noise ratio in the frequency spectra obtained from such samples is lower than for DTBN doped samples having a higher concentration of radical. No detailed comparisons of the frequency domain signal-to-noise ratios for various probes has been carried out.

A comparison, over a relatively wide temperature range, of Ω_c determined in the experiments reported here with Ω_c calculated on the basis of the literature values for

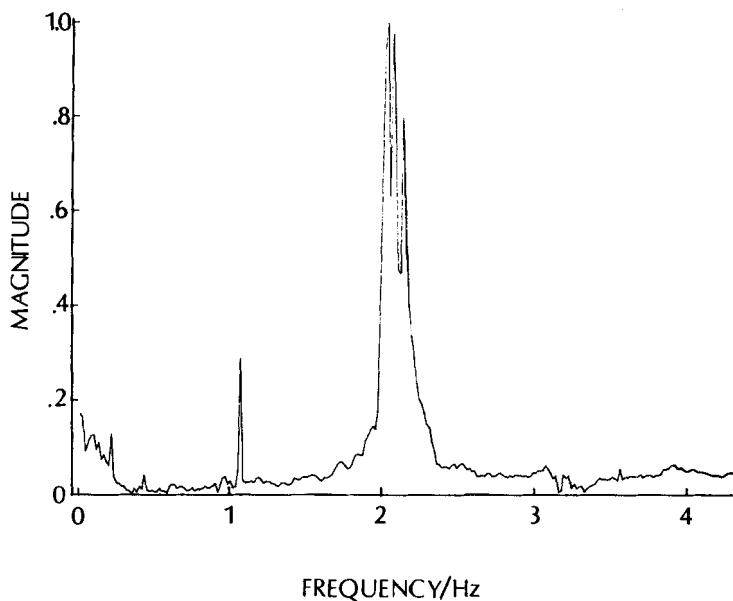


Figure 5. Frequency domain spectrum for 7×10^{-3} DTBN in Phase IV; $T = 318$ K, $\Omega = 1$ Hz, $H_0 = 3317$ G.

λ_1 and $\Delta\chi$ is possible in the case of Phase IV [7, 9]. A plot of $\Omega_c(\text{exp})$ versus $\Omega_c(\text{calc})$ for Phase IV over the temperature range 308 K to 344 K is linear with a least squares slope of 0.23 ± 0.02 and an intercept of 0.02 ± 0.02 Hz. This result provides strong support for the general form of equation (1) but indicates that either a factor of four is missing in the general equation or that there is an error in the experimental values for λ_1 or $\Delta\chi$. We have not, to date been able to resolve this question.

It is interesting to note that at temperatures below ~ 323 K the 2ω line in the frequency spectrum for both DTBN and VOAcAc in Phases V and IV is split by about 0.04 Hz (see figure 5). A similar effect was noted by LLS in their experiments on Phase IV. Figures 2 and 3 show that splittings are not observed in the frequency spectrum of DTBN in K15. It is suggested that microdomains, with slightly different director rotation frequencies, exist within the nematic Phase IV and V. If the minimum average lifetime of a spin probe within a microdomain is taken as the inverse of the splitting in the frequency spectrum, the Einstein-Smoluchowski equation can be used to calculate a value on the order of 10 microns for the minimum size of a microdomain.

Dr. F. Dowell made a number of helpful suggestions during the course of the experimental work and during the preparation of the manuscript. Mr. Thomas Mayhew assisted with some of the experiments and aided in the preparation of the manuscript. This research was supported by the Robert A. Welch Foundation of Houston, Texas.

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