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Orientation order and dynamics of $CDCl_3$ in ethylcellulose/chloroform liquid crystal phases

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Deuterium quadrupole echo spectroscopy has been used to probe the orientational behaviour and dynamics of $CDCl_3$ molecules in ethylcellulose/chloroform chiral nematic phases. The ^2H spectra of both left-handed and right-handed mesophases, formed by ethylcellulose with degrees of substitution of 2·3 and 3·0 respectively, were examined as functions of temperature and concentration. The observed quadrupolar splittings are relatively large and the magnitudes of the order parameters of the solvent molecules show little correlation with the handedness of the chiral phases. However, the ^2H line shapes of these two types of chiral phase exhibit rather different temperature dependences. Spectral simulations show that the observed line shapes and their temperature variations are mainly determined by diffusion of $CDCl_3$ molecules along the pitch axis. The effects of centrifugation on the ^2H spectra are also described.

1. Introduction

Many cellulose derivatives form lyotropic or thermotropic chiral nematic (cholesteric) liquid crystals under suitable conditions [1]. For lyotropic systems, both the mesophase formation and the handedness of the chiral nematics depend on the type of side chain substituents and the nature of the solvent [1, 2], indicating the importance of the side chain–solvent interactions. Furthermore, in mesophases formed by ethylcellulose (EC), the degree of substitution (DS) has been found to have a profound effect on the twist sense and temperature dependence of the pitch [3]. For example, it has been observed that EC samples having a DS value between 2·3 and 2·7 form, in chloroform, left-handed mesophases whose pitch decreases with increasing temperature, while fully substituted EC in chloroform yields right-handed mesophases whose pitch increases with increasing temperature. To elicit the molecular factors responsible for these macroscopic observations, orientational order and anisotropic motions of both side chain substituents and of solvent molecules in the mesophases must be examined. In a recent study of deuteriated ethyl substituents ($-CH_2-CD_3$) in the EC/chloroform

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mesophases, it was shown that two order parameters with different temperature dependences are required to describe the orientation of the polymer chain, and that an abrupt change in side chain conformations occurs within a certain concentration range [4]. In this work, we examine the behaviour of solvent $CDCl_3$ molecules in similar systems by deuterium magnetic resonance.

The ^2H NMR spectra are almost exclusively governed by the coupling between the nuclear quadrupole moment of the deuteron and the local electric field gradient tensor [5, 6]. In chiral nematics, where the orientation of the nematic director twists in space to form a helicoidal supermolecular structure, the fast fluctuations of molecular axes with respect to the director in each nematic layer lead to an averaged, or residual, field gradient tensor. In uniaxial liquid crystal phase, the magnitude of this residual field gradient tensor and its effect on the observed spectrum can be conveniently treated in terms of the order parameter of the C–D bond, S. Thus, the spectrum arising from $CDCl_3$ molecules of a particular nematic layer will consist of a doublet whose splitting $\delta\nu$ is given by

$$\delta\nu = (3/4)|S|(e^2qQ/h)(3\cos^2\Omega - 1) \tag{1}$$

where (e^2qQ/h) is the deuterium quadrupolar coupling constant and Ω the angle between the director and the external magnetic field. For an aliphatic C–D bond, the quadrupolar coupling constant is usually taken to be 170 kHz. The order parameter S is given by

$$S = \langle (1/2)(3\cos^2\theta - 1) \rangle, \tag{2}$$

where θ is the angle between the C–D bond and director of the nematic layer, and the angular brackets indicate an average over all intramolecular and reorientational motions. Since the C–D bond in chloroform is the unique C_3 symmetry axis of the molecule, S can also be considered as the order parameter describing the orientation of the solvent molecule with respect to the director. For randomly oriented samples the superposition of lines corresponding to an isotropic distribution of Ω values gives rise to the well-known Pake doublet for which the overall splitting is similarly proportional to the order parameter S. In equations (1) and (2), we assumed that the field gradient tensor is cylindrically symmetric about the C–D bond, and that the twisted nematic phases of $EC/CDCl_3$ are uniaxial [7, 8]. We also neglect molecular diffusion along the pitch axis, which, as shown later, has a profound effect on the observed spectra.

2. Experimental

Two different EC samples, EC of DS 2·3 and DS 3·0, were used in this study. The EC sample of DS 2·3 were purchased from Aldrich Co. (ethoxyl content 48 per cent, viscosity of 5 per cent solution in 80/20 toluene/ethanol 22 cP) and used without further purification. The EC sample of DS 3·0 was synthesized by alkylating EC of DS 2·3 with iodoethane in tetrahydrofuran [3]. The DS values were determined from the proton NMR spectra of isotropic solutions. The weight average molar masses are 65 000 and 62 000 for samples of DS 2·3 and DS 3·0 respectively. Circular reflectance spectroscopy measurements showed that they form mesophases of different handedness in chloroform; left-handed for EC of DS 2·3 and right-handed for EC of DS 3·0.

The spectra of four different $EC/CDCl_3$ samples were studied at different temperatures; the compositions were; 45·0 wt% EC of DS 2·3, 49·2 wt% EC of DC 2·3, 39·4 wt% EC of DS 3·0, and 44·4 wt% EC of DS 3·0. These concentrations were chosen to ensure the formation of anisotropic solutions [9, 10]. In terms of 'mole ratio' (mols of monomer units/mols of CDCl$_3$), the corresponding lowest and highest concentrations studied were 0·337 and 0·507. All samples were prepared by weighing appropriate amounts of EC and deuteriochloroform into 5 mm o.d.. NMR tubes and then sealing under vacuum. To aid dissolution, the tubes were kept at 40–50°C for several days to several weeks, depending on the concentration of the sample. Most samples exhibited typical cholesteric reflection colours. Repeated centrifugation in upright and inverted positions was originally employed to aid dissolution and to homogenize the viscous mixtures. However, it was found that this centrifugation process had a significant effect on the observed spectral pattern. Unless stated otherwise, the spectra shown and discussed below were obtained from samples prepared without centrifugation.

The ^{2}H NMR measurements were performed with a Varian XL-300 spectrometer operating at 46·1 MHz, using the phase alternating quadrupole echo sequence with a spectral width of 100 kHz. The 90 degree pulse was 9·5 μs in length and the separation time τ between two 90° pulses was varied from 30 to 500 μs. To obtain an acceptable signal/noise ratio, 1000–2000 quadrupolar echoes were accumulated.

The orientating effect of the magnetic field was investigated by keeping the sample in the field and recording spectra at different time intervals. During 10 hour overnight runs at 28·3°C, there was no detectable change in the recorded powder spectra for mesophases formed by EC of DS 2·3, but there was a small but noticeable increase in the relative intensity of spectrum wings for EC of DS 3·0, see figure 1. Similar (increasing relative intensity of the wings) but more noticeable changes were observed for both samples, if the temperature was first increased to 50°C and then returned to room temperature during the run. These results show that the magnetic field is not strong enough to orient the helicoidal structure of the cholesteric phase.

Spectral simulations were performed with a 386/33 MHz PC using a modified Wittebort program [11], and with the assumption that the samples consist of randomly oriented domains. To ensure that the experimental results correspond to such a random distribution, all spectra discussed below were recorded in the order of increasing temperatures. The procedure minimizes the effect of alignment which may take place at higher temperatures.

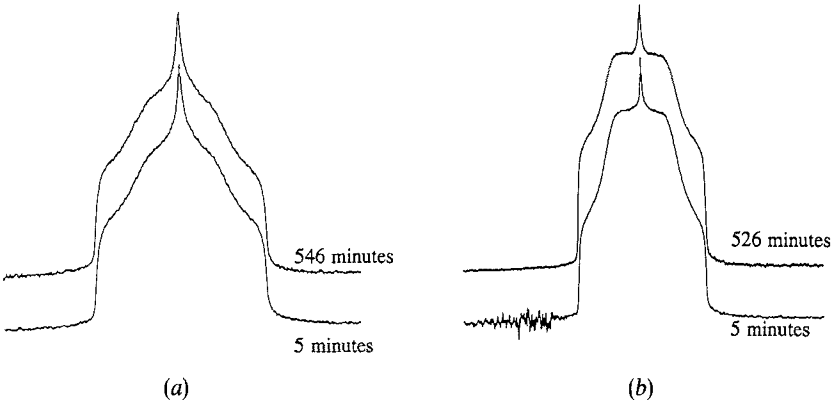


Figure 1. ^{2}H spectra recorded after samples had been in the magnetic field for the times indicated. The sample temperture was kept at 28·3°C during the experiment. The spectra show that the magnetic field has no significant effect on the observed spectra. (*a*) 45·0 wt% EC of DS 2·3 in CDCl$_3$: (*b*) 39·4 wt% EC of DS 3·0 in CDCl$_3$.

3. Results and discussion

Typical ^{2}H spectra recorded with different τ values are shown in figures 2 (*a*) and (*b*) for uncentrifuged and centrifuged samples respectively. In addition to the broader spectral pattern they also contain a narrow central component, which increases with increasing temperature and decreasing concentration. Similar narrow spectral components have also been observed in ^{2}H NMR spectra of deuteriated ethylcellulose/chloroform mesophases [4]. They can be attributed either to the more mobile regions, or to a small amount of isotropic phase formed from low molecular weight fractions of ethylcellulose. This interpretation is also consistent with the observed spectrum of mesophases prepared with low molecular weight EC of DS 2·3 (Aldrich Co., ethoxy content 48 per cent and viscosity of 5 per cent solution in 80/20 toluene/ethanol 4cP), see figure 3, which shows a much larger narrow centre peak. The ratio of integral areas of narrow and broad components also increases with temperature. Furthermore, the broader spectral component shows similar shape and width to those of the high molecular weight sample, while the narrow central component exhibits a rather wide base, indicating that the different molecular weight fractions yield spectra of different width. Fractionation of polydisperse cellulose derivatives has also been observed between the isotropic and anisotropic phases with the lower molar mass chain preferring the isotropic phase [12, 13].

Even neglecting the presence of narrow components, the spectra of these mesophases, see figure 2, are not the type of static or quasi-static powder pattern. It has been pointed out [14–17] that, due to the helicoidal structure of the cholesteric phase, the diffusion of molecules along the pitch axis results in a reorientation of the local director and therefore, an effective molecular reorientation with respect to the magnetic field, see figure 4 (*a*). Since for small solvent molecules in chiral nematics these

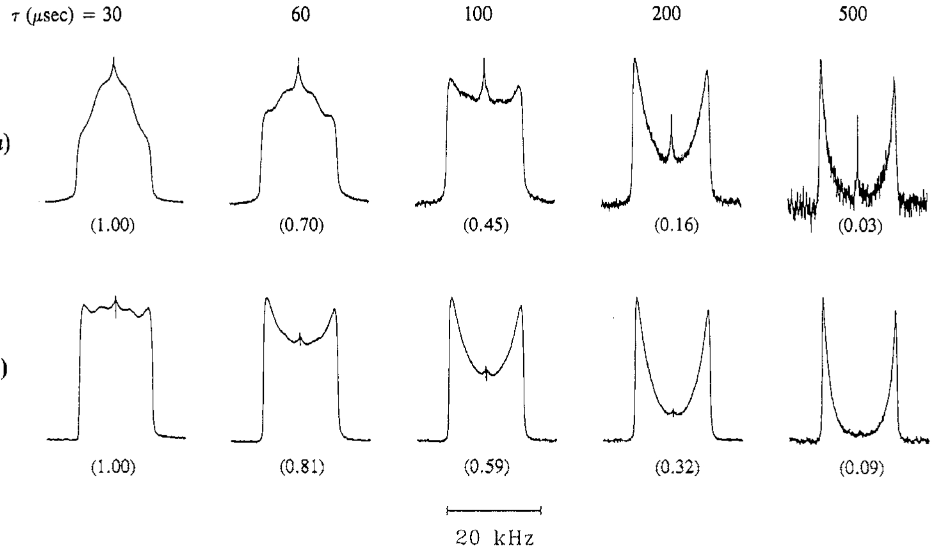


Figure 2. ^{2}H NMR spectra at 28·3°C, showing the dependence of the line shape on the pulse separation time τ. The number in brackets indicates the relative integrated intensity. (*a*) 49·2 wt% EC of DS 2·3 in $CDCl_3$, sample was prepared without centrifugation. (*b*) 50·1 wt% EC of DS 2·3 in $CDCl_3$, dissolution of EC was aided by repeated centrifugation in upright and inverted positions.

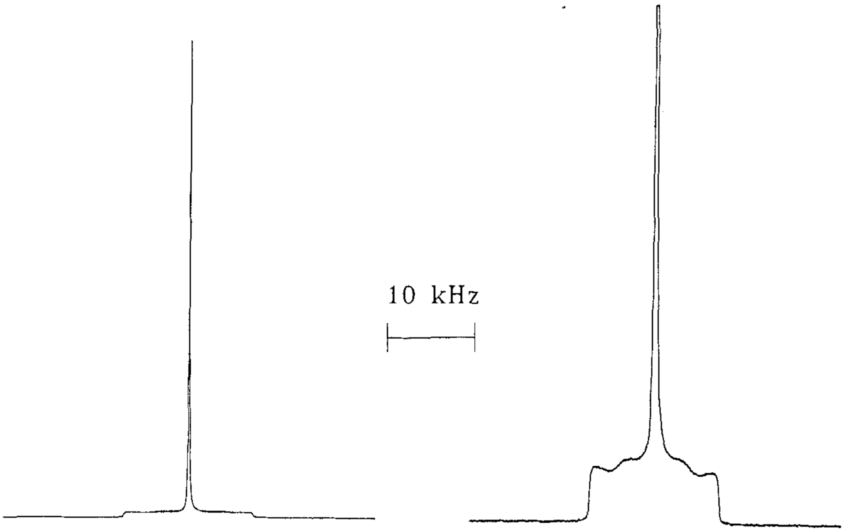
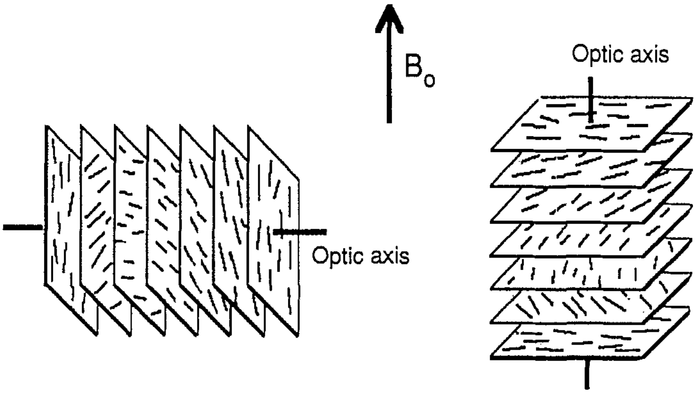


Figure 3. ^2H spectrum of 54·9 wt% low molecular weight EC in $CDCl_3$, at 28·3°C with $\tau = 30\,\mu s$. The right-hand side trace, plotted under higher amplification, shows more clearly the underlying broad component. To accentuate its broad feature, the sample had been centrifuged repeatedly in upright and inverted positions.



(*a*) (*b*)

Figure 4. Schematic representation of the helical twisted arrangement of the director with respect to magnetic field. (*a*) The pitch axis is perpendicular to the field B_0; (*b*) the pitch axis is parallel to the field B_0.

reorientational motions usually have rates of 10^4 to $10^6\,rad\,s^{-1}$ [15], which are comparable with the observed quadrupolar splittings, the observed line shape could be sensitive to the diffusion rate. In addition, the effect of diffusion on the director reorientation depends on the orientation of the domain's pitch axis with respect to the magnetic field. For example, in contrast to the situation shown in figure 4 (*a*), where the pitch axis is perpendicular to the magnetic field, figure 4 (*b*) shows that, for domains with their pitch axis parallel to the field, the direction of the director remains constant (= 90°) as the molecules diffuse along the pitch axis. Therefore, as shown in figure 2, the line shape is sensitive to the variation of τ, the pulse separation interval of the quadrupolar sequence. With increasing τ, the broad spectral pattern is expected to decay towards a doublet which mainly originates from domains having their pitch axis parallel, or nearly parallel, to the magnetic field. Spectral simulations (see below) lead to similar conclusions. Therefore, on the basis of simulated spectra, a small correction was made to the doublet splitting observed at the longest interval (500 μs) and the resulting value was used to derive the order parameters of $CDCl_3$, via equation (1), by taking $\Omega=(\pi/2)$. The S values thus obtained are plotted against temperature in figure 5. Considering the difference in concentrations, the magnitude of the solvent order parameters show little correlation with the twist sense of the mesophases.

The magnitude of the order parameters, $\approx 0{\cdot}1$, reflects an unusually strong solvent–polymer interaction. Much smaller solvent order parameters, usually in the range of 0·001 to 0·01, were observed for polypeptide based lyotropic twisted nematic phases [18, 19]. For example, for a PBLG-$CDCl_3$ solution with PBLG/$CDCl_3$ 'mole ratio' of 0·263, a quadrupolar splitting of 1·4 kHz was observed at room temperature [20], leading to an S value of $5{\cdot}5 \times 10^{-3}$. On the other hand, order parameters in the range of 0·1 were observed for $CDCl_3$ dissolved in thermotropic nematic hosts at concentrations of less than 10 mol% [21, 22]. In these thermotropic systems, $CDCl_3$ molecules are surrounded by rod-like nematic hosts and it is generally accepted that the shape anisotropy of the guest are mainly responsible for its orientation order [23–25]. Considering the large volume occupied by the $CDCl_3$ in our systems, it is unlikely that similar forces will play a dominant role in producing solvent order parameters of similar magnitude, and, therefore, a stronger solvent–polymer interaction of a different nature must be involved. This interaction probably causes the chain segments to straighten out and adopt an extended rigid conformation, leading to the formation of chiral nematic phases. In this respect, it would be interesting to study the solvent order parameters in other ethylcellulose based mesophases. Preliminary measurements on mesophases formed by EC of DS 2·3 in bromoform-*d* yielded solvent order parameters of similar magnitude.

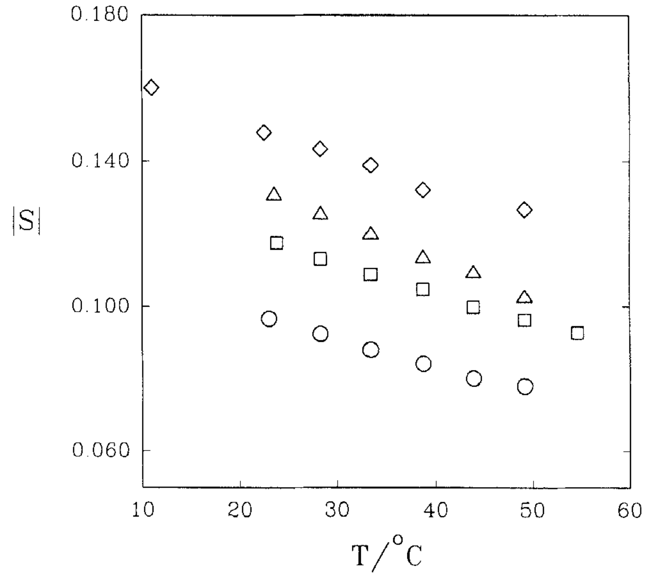


Figure 5. Variation of solvent order parameters with temperature, (◇) 49·2 wt% EC of DS 2·3, (△) 45·0 wt% EC of DS 2·3, (□) 44·4 wt% EC of DS 3·0 and (○) 39·4 wt% EC of DS 3·0.

As shown in figure 2, centrifugation has a profound effect on the observed spectral pattern. Furthermore, we also observed that the effect of centrifugation did not diminish during the course of the investigation (3–4 months), nor could it be eliminated or reduced by keeping the samples in a 50°C water bath overnight. The spectra of centrifuged samples, see figure 2 (*b*), exhibit higher intensity in the wings, and suffer less intensity loss with increasing τ. These features indicate the presence of more domains with their pitch axes parallel to the magnetic field. Thus we conclude that the shearing forces created by the centrifugation process allows domains to align with their helicoidal axes parallel to the axis of the sample tube, the direction of the magnetic field in a solenoid magnet. Centrifugation has also been found to affect ^2H spectral profiles of liquid-crystalline phases formed by aerosol OT [26, 27].

Figures 6 and 7 show deuterium NMR spectra ($\tau = 60\,\mu s$) of EC/$CDCl_3$ mesophases at several temperatures for EC of DS 2·3 and DS 3·0, respectively. Although the two sets of spectra have similar line shapes, they exhibit different temperature dependences. As the temperature increases, the spectral wings decrease in relative intensity for the DS 2·3 sample, see figure 6, but remain more or less unchanged for DS 3·0, see figure 7. As shown below, this difference can be associated with the temperature variation of the pitch and its effect on the $CDCl_3$ reorientation rate. In order to understand the effect of molecular reorientation on the observed ^2H line shape, simulated spectra were calculated for various reorientation rates, using the modified Wittebort program [11]. Since the program was intended for analysing the effect of jumping among discrete sites, the dynamic line shapes for our systems were computed by dividing the plane perpendicular to the pitch axis into 40 sites, or sectors, and modelling the reorientation diffusion process as discrete jumps between neighbouring sites [15, 28].

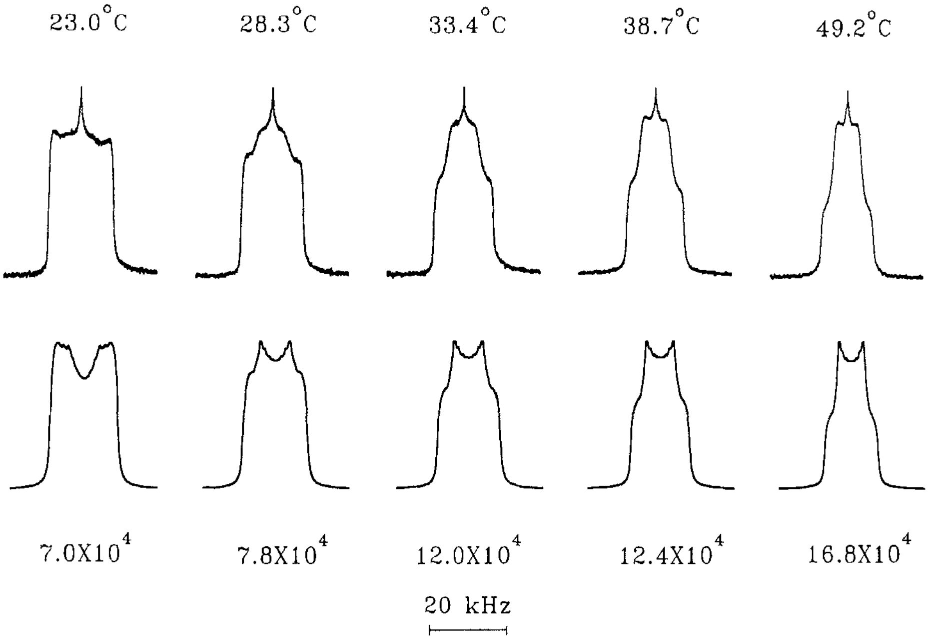


Figure 6. Experimental (upper) and simulated (lower) spectra of 49·2 wt% EC of DS 2·3 in $CDCl_3$ at different temperatures. The experimental spectra were obtained at the indicated temperatures with quadrupole echo sequence and $\tau = 60\,\mu s$. The simulated spectra were computed using the reorientation rates indicated in the figure.

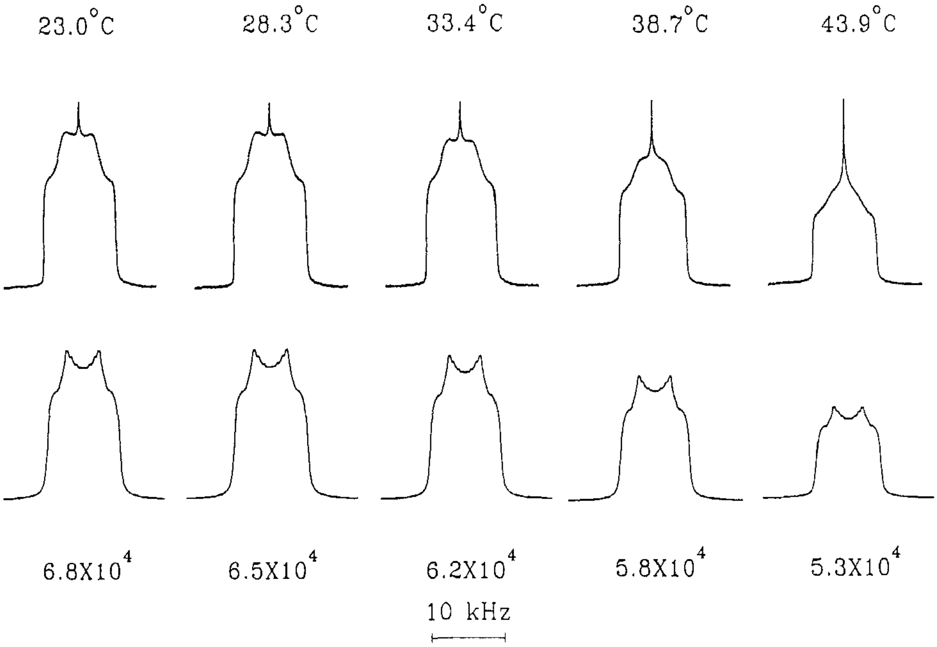


Figure 7. Experimental (upper) and simulated (lower) spectra of 39·4 wt% EC of DS 3·0 in $CDCl_3$ at different temperatures. The experimental spectra were obtained at the indicated temperatures with quadrupole echo sequence and $\tau = 60\,\mu s$. The simulated spectra were computed using .e reorientation rates indicated in the figure.

The simulated spectra, with the reorientation rates used in each simulation, are shown below the corresponding experimental spectra in figures 6 and 7. Except for the narrow central peak, which, as discussed above, is presumably caused by the low molecular weight fraction of EC sample, there is reasonable agreement between the simulated and experimental spectra. However, when this line-shape analysis was extended to spectra recorded at various pulse separation intervals τ, it was found that they could not be fitted with a single rate constant. Instead, for all the systems studied, the rate giving the best fit increased with increasing τ. Since dynamic processes in polymeric substances are known to involve a distribution of correlation times, attempts were made to fit the observed spectra by a superposition of line shapes for different reorientation rates, assuming a log–Gaussian distribution of rates [29, 30]. Although with variation of the distribution width, this procedure did reduce the discrepancies in most cases, we did not succeed in fitting the spectral patterns at different τ with a common set of dynamic parameters. It has been reported that the diffusion constants in chiral nematics decrease with observation time [31, 32], which would preduct a lower reorientation rate for longer τ. At present, the exact reason for the discrepancies is not known. They may be due to the assumptions involved in the spectral simulations. An isotropic distribution of domain orientations has been assumed and the chiral phase is taken as uniaxial. The possible distortion of the cholesteric helix in the presence of the magnetic field, as suggested by Vaz *et al.* [33], was not taken into consideration. It is known that domains in thick cholesteric samples usually adopt a focal conic texture, and the effect of curvature and of dislocations has been neglected. Thus the relatively fast translational diffusion of $CDCl_3$ molecules within each nematic layer of the twisted supermolecular structure would not lead to a change in the orientation of the directors.

Errors due to these assumptions cannot be eliminated by using a distribution of reorientation rates in the fitting procedure. It could be argued that the error caused by the presence of curvature and of dislocations is expected to increase with diffusion distance or with the pulse separation time τ. Furthermore, when assessing the effect of superposition of line shapes of different reorientation rates, it was observed that the procedure did not alter the general trend of the fitting parameters, i.e. the relative magnitude of the rates and their variations with temperature and concentration. In view of these considerations, the single rates which gave the best fit at the shortest τ ($=30\,\mu$s) were used for further evaluating the effects of the dynamic process.

In the table, the single rates, with the estimated errors, are listed for each of the systems studied. The values in the table indicate that CDCl$_3$ reorientation rates increase with temperature for EC of DS 2·3, but decrease with temperature for EC of DS 3·0, providing a rationalization for the different temperature variations of the deuterium resonance line shape observed for these two types of mesophases. At first glance it seems rather unusual that the reorientation rate would decrease with

Reorientation rate (R)†, pitch length (P_0)‡, and diffusion constant (D_p) of CDCl$_3$.

(A) 49·2 wt% EC of DS 2·3 in CDCl$_3$, left-handed

T/°C	11·0	22·5	28·3	33·4	38·7	49·7
$R/10^4\,\mathrm{rad\,s^{-1}}$	4·1	5·8	6·9	8·9	9·4	11·4
	(±0·9)	(±0·6)	(±1·1)	(±1·3)	(±1·6)	(±1·8)
P_0/nm	289	253	244	231	220	206
$D_p/10^{-11}\,\mathrm{m^2\,s^{-1}}$	4·3	4·7	5·2	6·0	5·7	6·2

(B) 45·0 wt% EC of DS 2·3 in CDCl$_3$, left-handed

T/°C	23·5	28·3	33·4	38·7	43·9	49·7
$R/10^4\,\mathrm{rad\,s^{-1}}$	5·3	6·4	7·6	9·1	9·9	10·6
	(±0·6)	(±0·9)	(±0·9)	(±1·0)	(±1·9)	(±2·7)
P_0/nm	317	308	295	283	276	265
$D_p/10^{-11}\,\mathrm{m^2\,s^{-1}}$	6·7	7·7	8·4	9·2	9·6	9·4

(C) 44·4 wt% EC of DS 3·0 in CDCl$_3$, right-handed

T/°C	23·8	28·3	33·4	38·7	43·9	49·7
$R/10^4\,\mathrm{rad\,s^{-1}}$	5·5	5·3	5·0	4·4	3·8	3·2
	(±0·7	(±0·7)	(±0·7)	(±0·5)	(±0·3)	(±0·3)
P_0/nm	364	388	424	473	531	601
$D_p/10^{-11}\,\mathrm{m^2\,s^{-1}}$	9·2	10·2	11·3	12·6	13·5	14·8

(D) 39·4 wt% EC of DS 3·0 in CDCl$_3$, right-handed

T/°C	23·0	28·3	33·4	38·7	43·9	49·7
$R/10^4\,\mathrm{rad\,s^{-1}}$	5·3	4·9	4·6	4·2	3·8	3·5
	(±0·7)	(±0·7)	(±0·5)	(±0·5)	(±0·4)	(±0·4)
P_0/nm	483	517	560	616	682	760
$D_p/10^{-11}\,\mathrm{m^2\,s^{-1}}$	15·7	16·7	18·2	19·9	22·2	25·6

† The estimated error is shown in brackets under the corresponding reorientation rate.
‡ The estimated error for P_0 is ±10 nm.

increasing temperature. However, we noted that the right-handed mesophases increase their pitch with increasing temperature [1], with the result that the $CDCl_3$ molecules must travel a longer distance to achieve the same degree of reorientation at a higher temperature. Based on the reflection wavelength data shown in figures 2 and 4 of [3] and assuming a value of 1·46 for the mean refractive index, the values of the pitch as a function of temperature have been estimated for each of the systems studied. The results are listed in the table. The diffusion constant D_p along the pitch axis can then be calculated by

$$D_p=(R/2)(p_0/2\pi)^2, \qquad (3)$$

where R is the reorientation rate in rad s^{-1}, and p_0 is the pitch length. The D_p values, listed in the table and plotted against temperature in figure 8, are within the range of $4{\cdot}0\times10^{-11}$ to $2{\cdot}6\times10^{-10}\,m^2\,s^{-1}$. Diffusion constants of similar magnitude have been reported for other nematic and chiral nematic phases [15–17, 34]. The present results indicate that much smaller diffusion rates occur in the left handed mesophases formed by EC of DS 2·3. However, in view of the difference in pitch lengths and in concentrations, no definite conclusions can be drawn concerning the relative mobilities of $CDCl_3$ in these two types of mesophases. The diffusion rate along the pitch axis has been observed to decrease rapidly with decreasing pitch length [16, 17, 32], thus inferring smaller D_p values for the tightly twisted left-handed chiral nematic phases examined in this study. In this regard, it is also of interest to note that the D_p values of right-handed mesophases exhibit larger relative increases with temperature, although

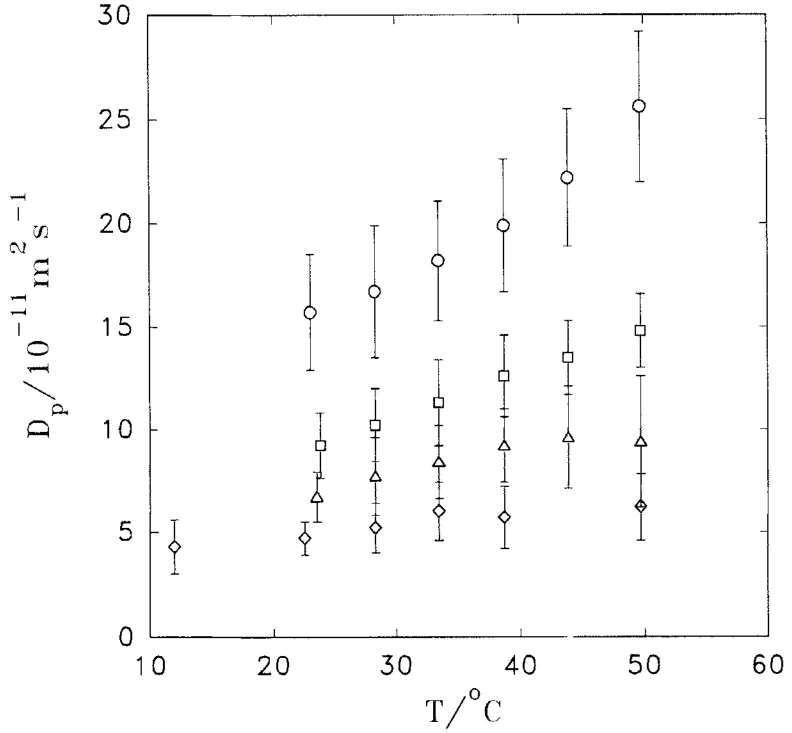


Figure 8. Temperature dependence of diffusion constants of $CDCl_3$. The error bars are based on the estimated uncertainties in R and P_0 values. (◇) 49·2 wt% EC of 2·3, (△) 45·0 wt% EC of DS 2·3, (□) 44·4 wt% EC of DS 3·0, (○) 39·4 wt% EC of DS 3·0.

their R values show a negative temperature dependence. For example, as the temperature was varied from room temperature to 49·8°C, increases of 61 per cent and 63 per cent in the D_p value were observed for the samples of right-handed mesophases, as compared with 42 per cent and 32 per cent increases observed for the left-handed mesophases. This difference in behaviours can be explained by recalling that, with increasing temperature, the pitch length of right-handed mesophases will increase, whereas that of left-handed mesophases will decrease. Thus, as the temperature increases, the increasing pitch facilitates, while the decreasing pitch retards the diffusion process, leading to the observed difference in the temperature dependences of their diffusion constants.

4. Conclusions

The magnitudes of the solvent order parameters suggest a strong polymer–solvent interaction in the ethylcellulose/chloroform chiral nematic phases. Spectral simulations were performed to examine the effect of molecular diffusion along the pitch axis. Although perfect fits between the simulated and experimental spectra obtained at different τs were not obtained, the simulation results yielded a consistent picture for the reorientation motion of CDCl$_3$ and its diffusion along the pitch axis. Thus, the variation of spectral patterns with temperature for mesophases of different twist sense can be related to the temperature dependences of their pitch.

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