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Molecular dynamics in the liquid crystal 40.6 A nuclear magnetic relaxation study

K. Venu^a; G. Ravindranath^a; V. S. S. Sastry^a

^a School of Physics, University of Hyderabad, Hyderabad, India

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Molecular dynamics in the liquid crystal 4O.6

A nuclear magnetic relaxation study

by K. VENU, G. RAVINDRANATH and V. S. S. SASTRY

School of Physics, University of Hyderabad, Hyderabad 500 134, India

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A nuclear spin lattice relaxation study of the liquid crystal butoxybenzylidene hexylaniline (4O.6) has been carried out as a function of Larmor frequency (4 to 30 MHz) and temperature covering all its mesophases (N, S_A and S_B), with a view to obtain information on different dynamic processes at the molecular level. These studies are also supplemented by a nuclear dipolar relaxation study as well as anisotropy of these relaxation rates with respect to the static magnetic field. The analysis of this data in nematic and smectic A phases based on a composite model, including the contributions from self diffusion (SD), order director fluctuations (ODF), and molecular reorientations (R), indicate that the nuclear spin relaxation is effectively mediated by diffusion and reorientation processes at frequencies above 10 MHz while at lower frequencies ODF also seem to contribute appreciably. The relative contribution from these mechanisms at different temperatures covering nematic and S_A phases are evaluated, and relevant dynamic parameters are calculated. The onset of the S_B phase is marked by sudden increase in T_1 and subsequent frequency independence of this data at lower temperatures. The dipolar relaxation data show a dramatic decrease at this transition temperature. These observations are attributed to a sudden slowing down of diffusion in the S_B phase.

1. Introduction

This paper reports the results of our N.M.R. studies on the liquid crystal butoxybenzylidene hexylaniline (4O.6) carried out as a function of temperature covering all mesophases and Larmor frequency (4 to 30 MHz). It is now established that the spin lattice relaxation rate (T_1^{-1}) in nematic phase reflects essentially three types of molecular mechanisms [1], viz. fluctuations of order director (ODF), molecular self diffusion (SD), and molecular reorientations (R). Each of these mechanisms leads, in principle, to a predictable frequency dispersion of the T_1^{-1} , and typical experimental data are normally a combination of all these three contributions to a first approximation. Investigation of the detailed frequency dispersion and of temperature variation of relaxation process to characterize these individual processes in a given liquid crystal is often an interesting and useful exercise. Typical Larmor frequencies that might be needed to do this study fruitfully cover a wide range, say from a few kHz to hundreds of MHz. However, there are systems in which even a limited range of study has been found to be sufficient to throw light on the dynamic processes [2, 3]. In particular, in butoxybenzylidene octylaniline (4O.8), proton T_1 measurements over a moderate range of frequency could indicate [2] that the relaxation was predominantly due to ODF. In this context, the present study aims at an investigation of related compound (4O.6), over a similar frequency range.

The frequency dispersion, anisotropy with respect to the static field and temperature dependence of the T_1 rates in 4O.6 indicate that the relaxation is diffusion

mediated in the higher frequency region while discernible contribution is present from ODF mechanism for Larmor frequencies below 10 MHz. By analysing the data with an appropriate composite model, the relative contributions of these mechanisms were estimated as a function of temperature in different phases and the appropriate parameters of molecular motions along with activation energies were evaluated. The earlier work aiming at an understanding of the critical behavior near the nematic (N) to smectic A (S_A) transition using detailed E.S.R. investigations was due to Zager *et al.* [4].

2. Experimental details

T_1 measurements were made on a home made pulsed N.M.R. spectrometer at different Larmor frequencies (4, 6.5, 10, 20, 25 and 30 MHz), using either the inversion recovery sequence or the saturation burst sequence [5]. The typical error in T_1 measurement is within 5 per cent. The temperature was controlled using a gas flow thermostat with a stability better than 100 m degrees. The dipolar relaxation times (T_{1D}) were measured using Jeener–Brokaert sequence [6] and are accurate to within 10 per cent.

The purified sample was obtained from elsewhere† and details of preparation were reported earlier [7]. The liquid crystal has the following phase sequence: $X \xrightarrow{33^\circ\text{C}} S_B \xrightarrow{49^\circ\text{C}} S_A \xrightarrow{64^\circ\text{C}} N \xrightarrow{79^\circ\text{C}} I$. The sample was sealed in vacuum after removing oxygen using standard procedure. All the measurements were made while cooling the sample from high temperature, and in the range 30 to 90°C. While making measurements in the smectic phases the sample was initially heated to the isotropic phase and was cooled very slowly to the required phase in the presence of a moderately strong magnetic field (10 kG). To minimize the temperature gradient across the sample, measurements were made with the sample immersed in a proton free liquid.

3. T_1 -process in liquid crystals

The spin lattice relaxation rate in liquid crystals can be adequately expressed as [8]

$$T_1^{-1} = T_{1ODF}^{-1} + T_{1SD}^{-1} + T_{1R}^{-1}, \quad (1)$$

in the region away from critical effects. The terms on the right hand side of this equation represent, respectively, contributions to the relaxation rate due to the ODF, SD and R mechanisms.

In a nematic phase, the orientational order (S) reaches essentially a constant value, and the important fluctuations then are orientations of this order (ODF) represented by

$$N(r, t) = N_0 + \delta N(r, t) \quad (2)$$

where N_0 is the average direction of the local orientations. These fluctuations can be described by an elastic free energy density due to the three deformations (splay, bend and twist represented by the constants k_1 , k_2 and k_3 respectively). Describing these fluctuations in the language of ‘ q -modes’ with wave vector dependent life times, the contributions to the relevant spectral densities at different frequencies, as seen by the nuclear spin can be calculated [8]. Out of the possible limiting cases arising due to the

† We thank Professor J. H. Freed of Cornell University for kindly providing the sample used in the present work.

comparison of the Larmor frequency (f) with the characteristic frequencies in the system, a physically realizable situation in most cases corresponds to f being much smaller than all important frequencies in the system. In such circumstances, the relaxation rate in nematic phase has the dispersion given by

$$T_{\text{ODF}}^{-1} = A\omega^{-1/2} \quad (\omega = 2\pi f). \quad (3)$$

The layer formation in the S_A phase can be represented by a complex order parameter $\psi(r)$, the modulus of which determines the density of the layers and the phase determines the relative position. The layer formation in the smectic phase does not allow bend and twist distortions (hence k_2 and k_3 diverge in the S_A phase) and as the transition temperature, T_{NA} , is approached from a higher value, cybotactic clusters form forcing a divergence of k_2 and k_3 . Thus T_1 is expected to show a critical behaviour as [9]

$$T_{\text{ODF}}^{-1} \propto (T - T_{\text{NA}})^x, \quad (4)$$

where x is an appropriate exponent.

The effect of the layer formation on T_1 process and the dispersion of relaxation rates for different limiting cases can be considered in detail [10, 11].

In case the diffusion mechanism is overwhelmingly effective in coupling the spins to the lattice, the frequency dispersion caused by the ODF as well as the pretransitional behaviour near T_{NA} as indicated above, are normally suppressed. Diffusion is theoretically investigated based on Torrey's theory for liquids [12, 13] and subsequent extensions to liquid crystals. Zumer *et al.* [14] and Vilfan *et al.* [15] have extended this theory by considering the diffusion of elongated cylindrical shape molecules with a chosen distribution of spins on the cylindrical surface in a perfectly oriented system. It can be argued that the relaxation rate in nematics, then, is expressible as

$$T_{\text{ISD}}^{-1} = \frac{2}{3}(\gamma^2 \hbar)^2 \frac{\eta \tau_{\perp}}{d^3} Q \left(\omega \tau_{\perp}, \frac{\langle r_{\perp}^2 \rangle}{d^2}, \frac{D_{\parallel}^0}{D_{\perp}^0} \right). \quad (5)$$

Here, η is the spin density, γ is the gyromagnetic ratio, $\langle r_{\perp}^2 \rangle$ is the mean square molecular jump length perpendicular to the long molecular axis, d is the diameter of the cylindrical molecule, D_{\parallel}^0 and D_{\perp}^0 are the microscopic self diffusion constants of perfectly ordered phase in the directions parallel and perpendicular to the long molecular axis, and τ_{\perp} is the correlation time associated with the diffusion in the direction perpendicular to the molecular axis which is given by

$$\tau_{\perp} = \frac{\langle r_{\perp}^2 \rangle}{4D_{\perp}^0}, \quad (6)$$

The function Q above is dimensionless and can be evaluated only numerically. A similar expression for the S_A phase can be obtained [15] with an additional parameter l/d in the argument of Q (l is the length of the molecule). The angular dependence of T_1 can also be included in the above function Q .

However, contributions to the relaxation due to the diffusion in the typical frequency range commonly in the N.M.R. experiments is found to be quite satisfactorily accounted for, by the Torrey's theory itself, but for a scale factor of 1.4 [14, 15]. In such a case the relaxation rate can be expressed as

$$T_{\text{ISD}}^{-1} = \frac{1}{1.4} T_{1\text{TORREY}}^{-1}. \quad (7)$$

In addition to these two mechanisms, represented by equations (3) and (7), considerable contribution to T_1^{-1} often comes from reorientational motions. The rotations of the molecules around their long axes, fast isotropic reorientational motions of aliphatic chains, and orientational fluctuations of the molecular axes are, in principle, to be accounted for by the superposition of lorentzian distributions, but the experimental time scales employed restrict their contribution to a temperature dependent constant, independent of frequency.

Thus the total relaxation rate can be expressed as

$$T_1^{-1} = \frac{1}{1.4} T_{1\text{TORREY}}^{-1} + A\omega^{-1/2} + B, \quad (8)$$

where B is a frequency independent term with contributions from rotational motions. Details of calculations of contribution from diffusion based on Torrey's model are available [12].

4. Results

Variation of T_1 as a function of temperature in the present system is shown in figure 1 at two frequencies (10 and 30 MHz). Salient features of this data are: pretransitional behaviour near T_{IN} , discontinuous jump of T_1 at T_{IN} , decrease of T_1 with decrease in temperature in the nematic phase, no appreciable change in T_1 near T_{NA} , considerable decrease of T_1 with temperature in a smaller temperature region covering the S_A phase, pretransitional behaviour near T_{AB} , large jump in T_1 at T_{AB} and

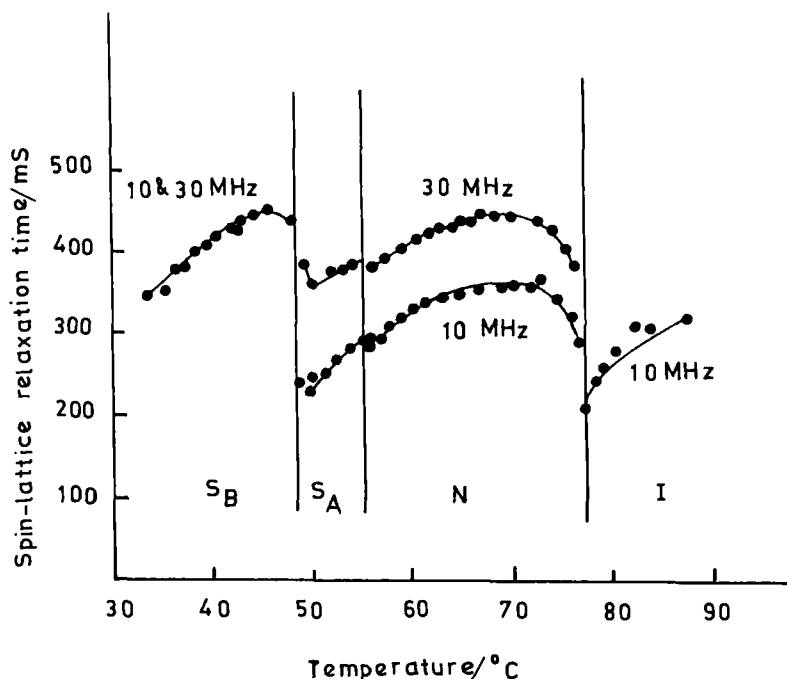


Figure 1. Spin lattice relaxation time (T_1) as a function of temperature (T) in 4O.6 at two frequencies (10 and 30 MHz). Solid lines are drawn to provide guide to the eye. Vertical lines show the transition temperatures from one phase to another.

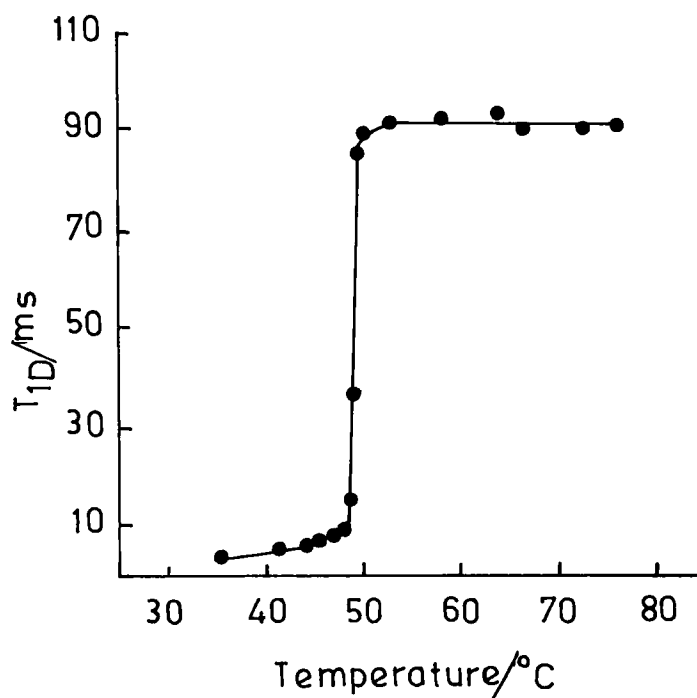


Figure 2. Dipole relaxation time (T_{1D}) as a function of temperature in 4O.6. Solid line is drawn to provide guide to the eye.

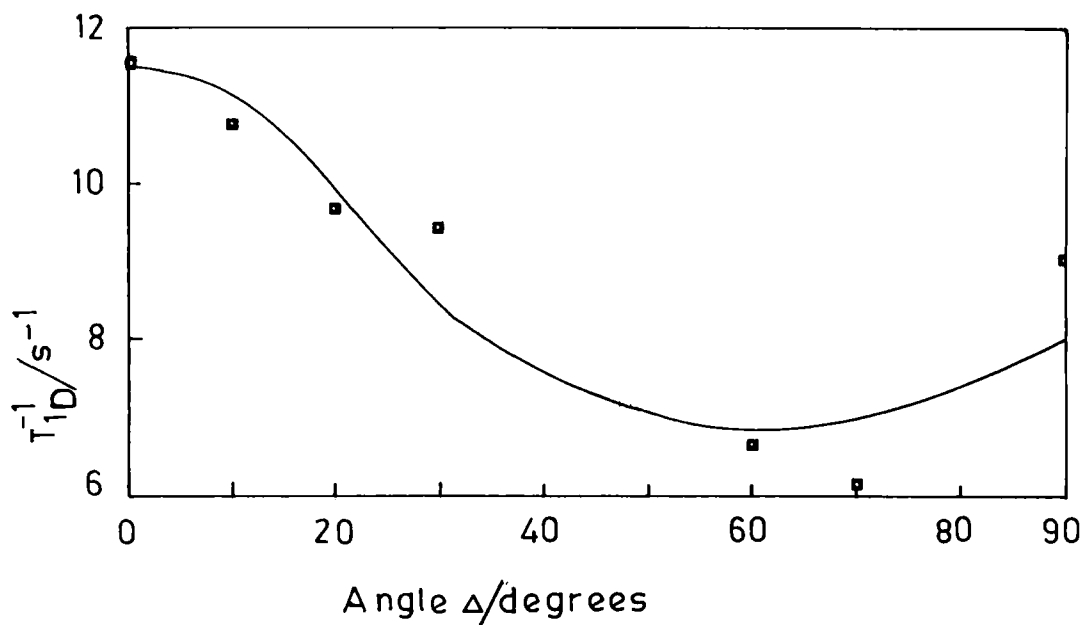


Figure 3. Dipolar relaxation rate (T_{1D}^{-1}) as a function of angle (Δ) between the magnetic field and the director in S_A phase of 4O.6. Solid line is the best fit curve to equation (12).

decrease of T_1 with decrease of temperature in S_B phase without showing any frequency dependence. The variation of T_{1D} with temperature is shown in figure 2. Variation of T_{1D} with the angle (Δ) between the magnetic field and the director in S_A phase is shown in figure 3.

It is observed that the frequency dependence of T_1 in this compound is not consistent with equation (3) indicating the necessity to include contribution from mechanisms other than the ODF. In order to calculate T_1 due to diffusion from equation (7), T_1^{-1} can be expressed as [12]

$$T_{1\text{TORREY}}^{-1} = \frac{4}{3}\pi\gamma^4\hbar^2 I(I+1) \frac{\eta}{d^3\omega} \phi(\alpha, x). \quad (9)$$

Here I is the spin of the nucleus. The function $\phi(\alpha, x)$ can be evaluated knowing

$$\alpha = \frac{\langle r^2 \rangle}{12d^2}$$

and

$$x = \left[\frac{\omega d^2}{D} \right]^{1/2}.$$

The mean squared flight distance used in the diffusion model is represented by $\langle r^2 \rangle$ above, and the diffusion coefficient D is related to mean time between flights, τ , as

$$D = \frac{\langle r^2 \rangle}{6\tau}, \quad (10)$$

Torrey's model, meant for isotropic diffusion, is also a good approximation for anisotropic phases (nematic and smectic A), as far as frequency dispersion data covering the normal N.M.R. frequency range are concerned (but for a scaling factor 1.4 as indicated in equation (7)). Typical choices made for various parameters to use this model for nematic phase are $D = D_{\perp}^0$, $D_{\parallel}^0/D_{\perp}^0 = 2$, $\langle r^2 \rangle = \langle r_{\perp}^2 \rangle$ [14]. It is further assumed that the two mean residence times τ_{\parallel} and τ_{\perp} are equal and can be substituted in Torrey's model for τ , i.e. $\tau = \tau_{\parallel} = \tau_{\perp}$. The anisotropy in the diffusion as chosen by the above ratio is typical for a nematic phase, and this ratio does not affect the dispersion data to any appreciable extent [14, 15].

Contributions from diffusion in the nematic phase are thus calculated by analysing the frequency dispersion at various temperatures based on equations (7) and (9), using τ as the variable parameter to achieve the best fit. The other numerical data substituted in the equation are: $n = 5 \times 10^{22}$ spins/cm³, $\langle r_{\perp}^2 \rangle = \langle r^2 \rangle = d^2 = 25 \text{ \AA}^2$. Anisotropy of the relaxation data with respect to the angle Δ is another departure from the Torrey's model, though such studies are not readily possible in the nematic phase. Application of this procedure to the S_A phase requires recognition of the fact that there are now two distinct resident times τ_{\parallel} and τ_{\perp} and the Torrey's model is a very good approximation for frequency dispersion in this case provided, (i) magnetic field is parallel to the director, and (ii) $\omega\tau_{\perp} > 0.3$. The experimental data in the S_A phase has been analysed keeping these requirements in view, with τ_{\perp} as the variable parameter. Further, the anisotropy of T_1 with respect to Δ is also studied at two different frequencies (10 and 30 MHz) in the S_A and S_B phases. Figure 4 shows T_1 variation as a function of Δ at 10 MHz in the S_A and S_B phases. 30 MHz data also shows a similar variation.

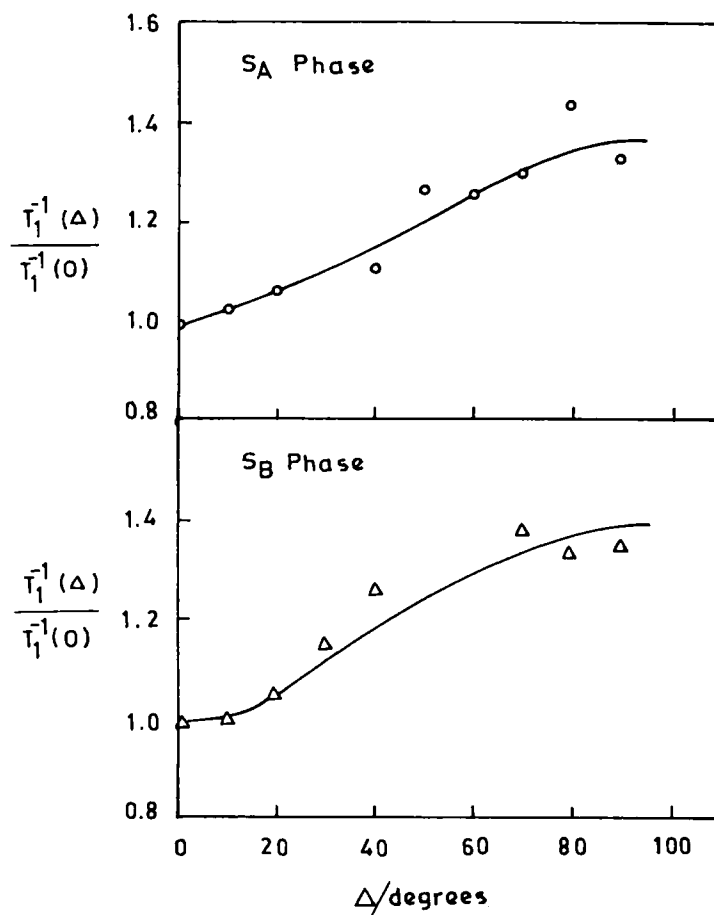


Figure 4. Relative variation of spin lattice relaxation rate $T_1^{-1}(\Delta)/T_1^{-1}(O)$, as a function of angle (Δ) between the magnetic field and the director in the S_A and S_B phases 4O.6 as measured at 10 MHz. Solid line is to provide guide to the eye.

It may be noted that even this analysis based on diffusion does not fit the dispersion data adequately at any of the temperatures (covering the N and S_A phases). Apparently, there is a contribution both from ODF and SD to the observed frequency dispersion, apart from a possible role for reorientations leading to frequency independent term. It is clear from the above discussion that the diffusion mechanism in these anisotropic phases is best represented by Torrey's model at relatively higher Larmor frequencies, whereas ODF should be dominant at lower frequencies. Keeping this in view, the data in the frequency range 10 to 30 MHz are first analysed using Torrey's model. The fit at all the temperatures for this frequency interval is very good and this indicates that SD and R mechanisms are sufficient to account for T_1 rate at Larmor frequencies higher than 10 MHz. Extrapolating these contributions for frequencies down to 4 MHz, the ODF contribution is recovered as the difference between the observed and expected rates. The results of such an analysis at a typical temperature in the nematic phase is shown in figure 5. The diffusion data recovered from the experiment permits us to calculate the D_1^0 at each temperature in both these phases and the variation of this coefficient with temperature is shown in figure 6. Assuming a thermally activated diffusion mechanism based on Arrhenius model, the data in

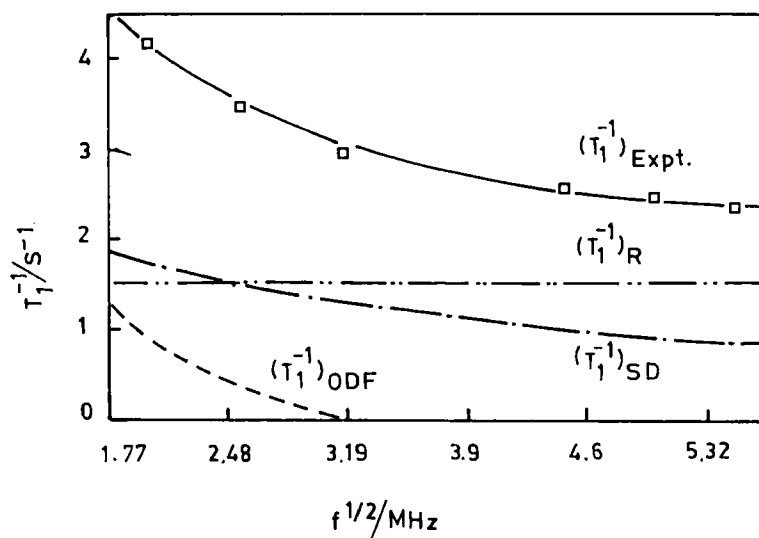


Figure 5. Variation of spin lattice relaxation rate (T_1^{-1}) as a function of square root of Larmor frequency (f) in nematic phase of 40.6. Contributions to relaxation time from self diffusion (T_{SD}^{-1}), reorientations (T_{R}^{-1}) and ODF (T_{ODF}^{-1}) as a function of frequency, obtained from the analysis as explained in the text are also shown in this figure.

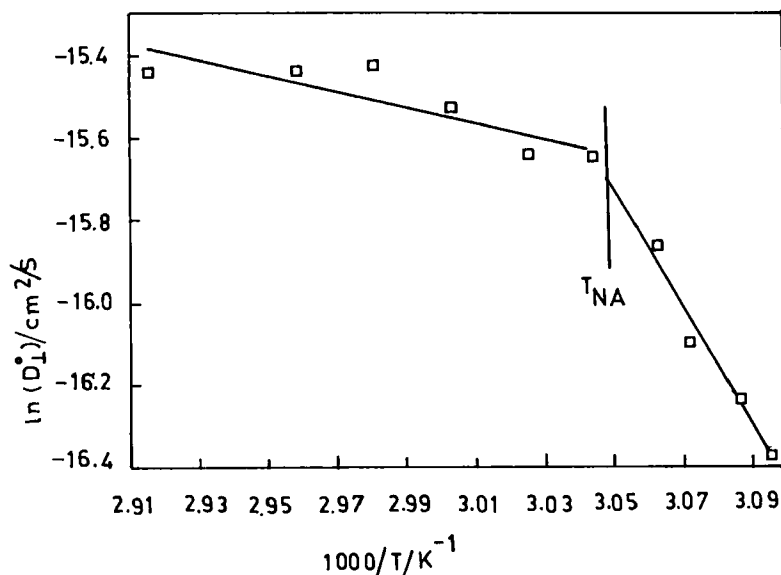


Figure 6. Arrhenius plot of the macroscopic self diffusion coefficient in the direction perpendicular to the long molecular axis (D_{\perp}^0) in the nematic and smectic A phases of 40.6. The solid lines are the best fit curves.

figure 6 can be used to calculate the activation energy for diffusion in both these phases, as 3.6 ± 0.5 cal/mole (nematic phase), and 28.2 ± 1 kcal/mole (S_A phase).

The relaxation rate due to reorientations in all these mesophases is also temperature dependent. There are three types of reorientations one should consider for these type of molecules [16]. They are (i) reorientations of the molecules along their long molecular axes (ii) reorientations of the molecules along their short molecular

axis and (iii) the isotropic reorientation of the aliphatic end chains. In liquid crystals, reorientations around long molecular axis are normally very fast and hence their contribution to the relaxation process (T_{IRL}^{-1}) is considered to be very small. In the N and S_A phases even the isotropic reorientation of end chains is very fast and hence their contribution to T_1 process (T_{IRI}^{-1}) is considered to be negligible. In fact, only the reorientations around the short molecular axis are normally taken into account in nematic and smectic A phases [16], and their contribution (T_{IRS}^{-1}) is written as

$$T_{\text{IRS}}^{-1} = 5\varepsilon C' \tau_s, \quad (11)$$

in $\omega\tau_s \ll 1$ limit. ε here represents the anisotropy of these motions and τ_s is the correlation time associated with the reorientation around short axis. Here the constant C' is given by

$$C' = \frac{2}{8} \gamma^4 \hbar^2 \frac{1}{13} \sum_k u_k (3l_k^2 - 1)^2 / r_k^6, \quad (12)$$

where u_k is the relative weight of protons belonging to k th group, $l = 1$, $r_k = 2.44 \text{ \AA}$ and $u_k = 8/31$ for benzene ring and $l = 0$, $r_k = 1.78 \text{ \AA}$, and $u_k = 22/31$ for CH_2 and CH_3 groups.

In the ordered smectic phases, the rotation around short molecular axis freeze the contribution to T_1 , comes mostly from reorientation of tails [16] which can be written as

$$(T_1^{-1})_R = \frac{22}{31} \frac{3}{2} \frac{r^4 \hbar^2}{r^6} \tau_c,$$

in the $\omega\tau_c \ll 1$ limit, where ω_c is the correlation time associated with isotropic reorientations of the end chains.

In the light of the above discussion the frequency independent portion obtained from the above analysis is attributed to reorientations around the short molecular axis

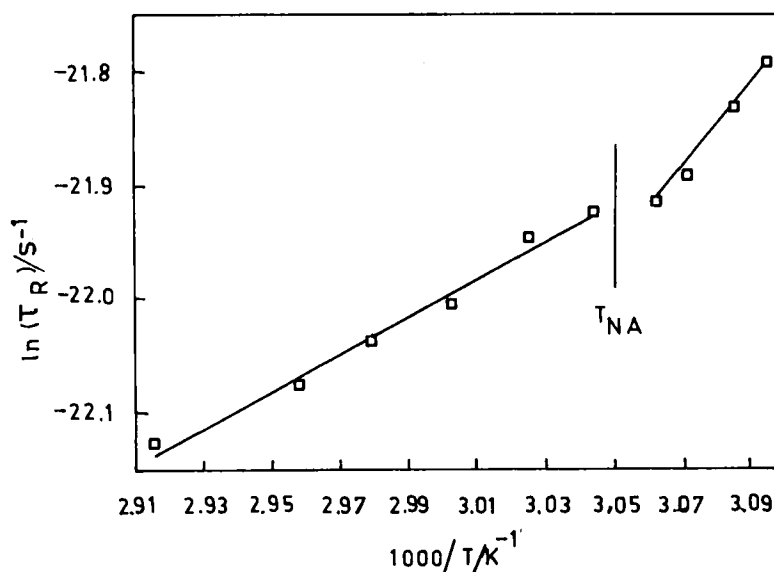


Figure 7. Arrhenius plot of the correlation time associated with reorientations ($\tau_R = \tau_s$) in the nematic and smectic A phases of 4O.6. The solid lines are best fit curves.

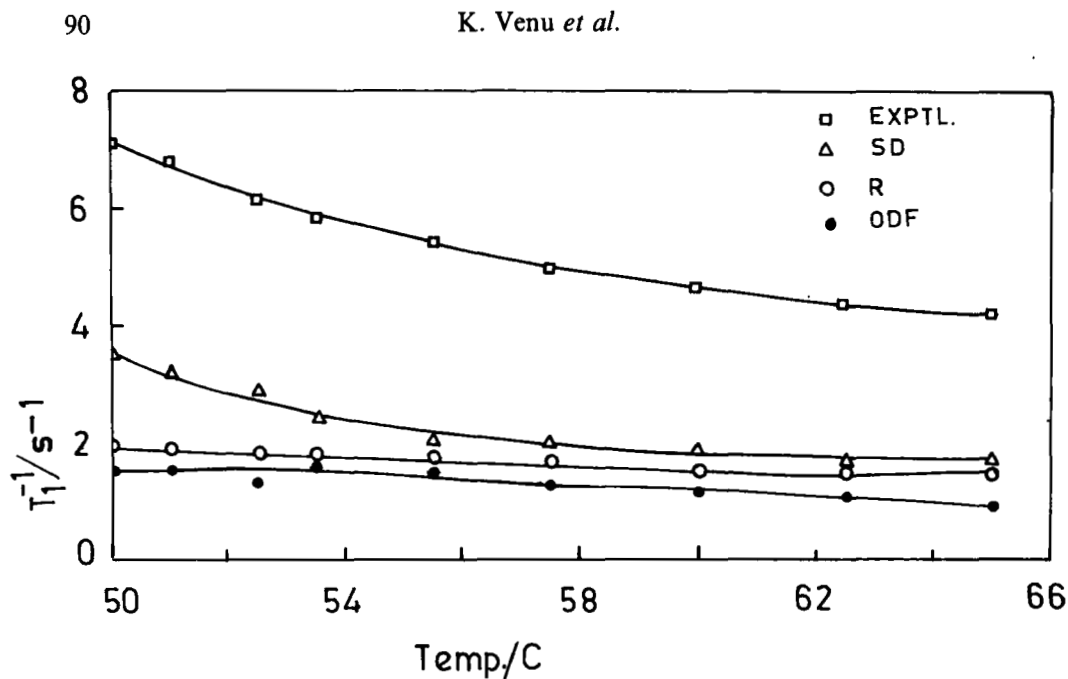


Figure 8. Variation of T_1^{-1} , T_{ISD}^{-1} , T_{IODF}^{-1} and T_{IR}^{-1} as function of temperature in the nematic and smectic A phases of 4O.6 at 4 MHz.

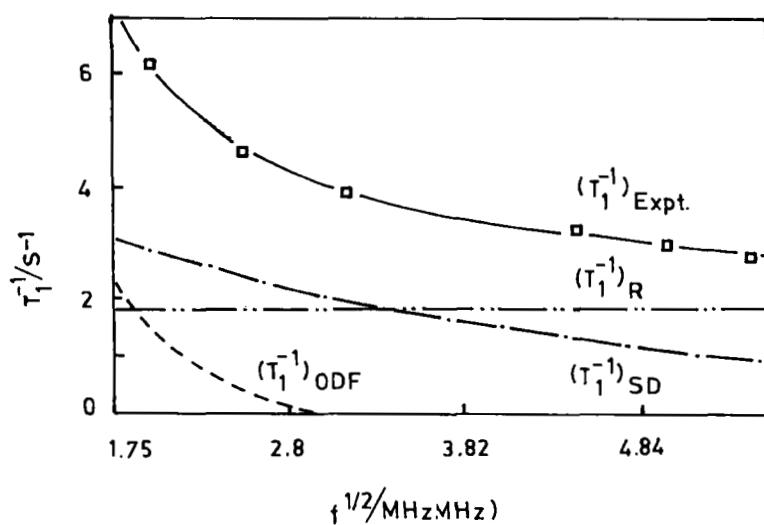


Figure 9. Variation of spin lattice relaxation rate T_1^{-1} as a function of square root of Larmor frequency (f) in the smectic A phase of 4O.6. Variation of T_{ISD}^{-1} , T_{IR}^{-1} , T_{IODF}^{-1} , as a function of frequency is also shown in this figure.

in the N and S_A phases and the data is accordingly fitted to equation (11) and (12) assuming these reorientations to be isotropic ($\varepsilon = 1$). The typical value of τ_s thus obtained is 3×10^{-10} s, which agrees with τ_s values obtained earlier in similar type of compounds [3, 16]. From the temperature dependence of τ_s (figure 7) obtained by repeating the analysis at other temperatures in the N and S_A phases, the activation energy associated with these rotations assuming them to be thermally activated, is

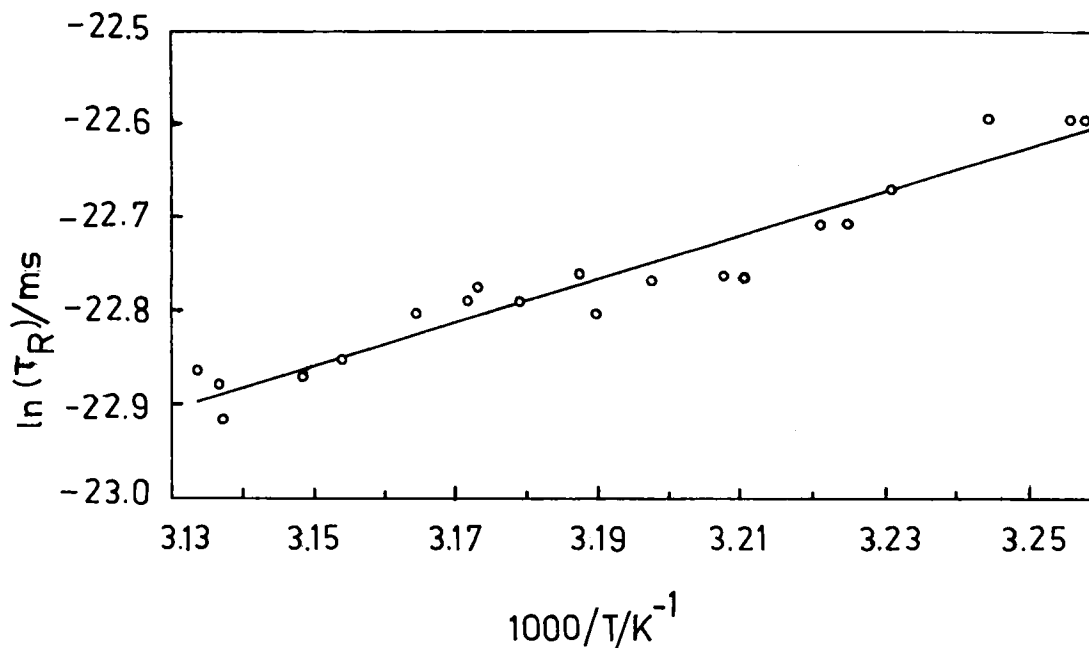


Figure 10. Arrhenius plot of correlation time associated with reorientations ($\tau_R = \tau_C$) in smectic-B phase of 4O.6. The solid curve is the best fit line.

found to be 3.3 ± 0.5 kcal/mole and 7.3 ± 0.5 kcal/mole in the N and S_A phases respectively.

The T_1 data in the S_B phase is frequency independent and hence is entirely due to reorientations in $\omega\tau_c \ll 1$ limit. As discussed above, in this phase the most dominating mechanism is due to the isotropic reorientation of the end chains. The T_1 data in this phase is now fitted to equation (13) to obtain the correlation time associated with these motions (τ_c). The typical value of τ_c , thus obtained is 1.4×10^{-10} s which is of the order of similar measurement in the ordered smectic phase of a similar compound [16]. From the temperature dependence of the τ_c (figure 10) the corresponding activation energy is found to be 4.7 ± 0.5 kcal/mole in the N and S_A phases respectively.

5. Discussion

It has been possible to estimate the relative contributions from the three mechanisms to the T_1 process, at different temperatures, using the present study. The strong deviation of the data at low frequencies from the diffusion model is a direct pointer to the onset of ODF, which are expected to couple effectively at lower Larmor frequencies. From this ODF contribution the typical value of A in equation (8) is computed to be about $6000 \text{ s}^{-3/2}$ in nematic phase. Variation of different contributions making up for the observed relaxation rates as a function of temperature at 4 MHz is plotted in the figure 8.

The present study may be compared with a similar work on 4O.8 [2]. Relaxation data over a similar limited Larmor frequency range in that compound indicated the dominance of ODF mechanism in the nematic range with a very fast self diffusion ($\omega\tau \sim 10^{-3}$). The temperature dependence of T_1 in 4O.8 also supports this explanation indicating gradual expulsion of certain elastic distortions as T_{NA} is reached from

above. In contrast, a closely related compound like 4O.6 with a shorter end chain length seems to have a much slower diffusion ($\omega\tau \sim 1$), thereby effectively mediating the nuclear relaxation process in the higher frequency region. The observation of the effect of ODF mechanism at lower frequencies, in a study which employed only moderate frequency range, is rather a fortuitous circumstance and hence permits one to estimate all major contributions.

T_1 data in the present system shows a small (about 5 per cent) jump near T_{NA} at all the frequencies (figure 1), and this is reproducible. From consideration of critical fluctuations near T_{NA} , the gradual expulsion of bend and twist distortions, as the S_A phase is formed, would lead to anomalous increase in the T_1 value (equation (4)), as observed in certain systems [12, 3]. However, a competing diffusion mechanism with a strong temperature dependence in the opposite sense is normally found in systems, obscuring the effect of ODF. The presence of a small but consistent jump near T_{NA} in the present liquid crystal could then be attributed to the fact that very near T_{NA} , the ODF contribution is reduced substantially enough to pull the resultant T_1 value up perceptibly. This observation is consistent with the result that ODF mechanism does contribute to T_1 in this phase, though effectively only at lower frequencies.

In the S_A phase there are few other possible mechanisms responsible for relaxation [10]. Smectic order fluctuations will normally give rise to the same frequency and angular dependences of T_1 as those due to ODF in the nematic phase. Smectic undulation waves result in a f^{-1} dependence of T_1^{-1} . Finally, diffusion induced ODF yields a frequency dependence as that of the ODF mechanism. However the data in S_A phase has very similar features compared to nematic phase and hence rule out the above possibilities (figure 9). It is concluded that diffusion continues to effectively mediate the relaxation processes in the S_A phase also. The activation energy (28.2 kcal/mole) in the S_A phase, however, is greater than that in the N phase (3.6 kcal/mole) pointing out to the hindrance for diffusion in the S_A phase brought about by the partial translational ordering (layer formation).

The observed anisotropy of T_1^{-1} in the S_A phase is difficult to assign quantitatively. It is expected that there should be very little anisotropy due to diffusion at the observed diffusion rates (i.e. $\omega\tau_c \sim 0.1$ to 0.7) and T_1^{-1} is at best expected to decrease with angle slightly, rather than show an increase. The ODF mechanism could be partially responsible for this angular dependence. There is also contribution from reorientational motion [1] which has qualitatively a similar angular dependence as observed. However assignment of relative roles of these mechanisms to account for the experimental data is rather difficult owing to the lack of precise information on molecular details.

The jump in T_1 near T_{AB} is due to the sudden slowing down of the diffusion, consequent to the onset of translational order within the layer in the S_B phase. The T_1 data do not show any frequency dependence in this phase within experimental error and shows, on the other hand, a strong Arrhenius type temperature dependence. As is discussed earlier this leaves the reorientations as the possible mechanism mainly mediating the relaxation process in the limit $\omega\tau_R \ll 1$. The anisotropy of T_1 data in this phase is very similar to the S_A phase (figure 4). However, no attempt has been made to make a comparison of these two results due to reasons already mentioned.

The dipolar relaxation process (T_{1D}) is sensitive to spectral densities at very low frequencies and the sudden freezing of molecular motions in the S_B phase leads to efficient coupling of T_{1D} process with the lattice. The steep drop in T_{1D} (figure 2) near T_{AB} can thus be understood. T_{1D}^{-1} can be related to the correlation times of these slow

motions, in the strong collision limit, as

$$T_{1D}^{-1} = \frac{2(1-p)}{\tau_c}, \quad (14)$$

where $(1-p)$ is a calculable geometric factor, of the order of unity [17]. While it is difficult to know this factor exactly, an upper limit of the correlation time can still be obtained to be 20 ms. A translational diffusion in the S_B phase with this typical correlation time will have a coefficient in the range of 10^{-12} cm²/s.

The observed orientation dependence of T_{1D} in the S_A phase (figure 3) is very much different from that of T_1 in the same phase (figure 4). This means that the spectral density function $J_2(2\omega)$ is not contributing appreciably to T_{1D} mechanism in the S_A phase [18]. In that case, if T_{1D} process is assumed to be due to the ODF mechanism, dipolar relaxation rate, in the weak collision limit, can be written as [22]

$$T_{1D}^{-1} = C_0 J_0(0) + C_1 J_1(\omega) \quad (15)$$

where C_0 and C_1 are constant and $J_0(0)$ and $J_1(\omega)$ are the spectral density functions associated with ODF at zero and Larmor frequencies. In this limit, the angular dependence of dipolar relaxation rate can be written as

$$T_{1D}^{-1} = ah(\Delta) + b, \quad (16)$$

where a and b are constants and $h(\Delta) = (C_0/C_1)f_0(\Delta) + f_1(\Delta)$ and $f_0(\Delta) = 18(\cos^2 \Delta - \cos^4 \Delta)$ and $f_1(\Delta) = (1/2)(1 - 3\cos^2 \Delta + 4\cos^4 \Delta)$. The experimental data is fitted to equation (16), using least square method which yielded a value of $C_0/C_1 = 1/65$.

Figure 1 shows appreciable pretransitional behaviour of T_1 near T_{AB} over a range of about 2°C above the transition temperature at all the frequencies, and similar effects are noticed in 4O.8 also [2]. It may be noted that this transition is interpreted based on melting theories of 2-dimensional solids [19, 20, 21, 22], and it is suggested that there could be two transitions connected with this melting process, first transition (T_{AB}) being associated with dislocation mediated melting while the other (at T') involving the order parameter of the transition. But since the S_B phase does not represent a true 2-dimensional solid (due to finite correlation between layers), it is argued that there may be a crossover between 2d and 3d melting behaviour resulting in a first order transition (at T_{AB}) with pretransitional effects [23]. This present observation lends support to such possible interpretation, as is the case with 4O.8. But in 4O.8, these effects were interpreted as due to further expulsion of the bend and twist distortions in the S_A phase as T_{AB} is reached and is consistent with the picture that ODF was the dominating mechanism for T_1 process in that system. However such a conjecture cannot be made unambiguously in the present case, as diffusion is found to be primarily responsible for T_1 process in S_A also. It may also be noted that the T_{1D} process which is sensitive to the onset of any slow motions in the medium does not show any pretransitional behaviour till the sudden drop at T_{AB} .

6. Conclusions

All the three important mechanisms (SD, ODF and R) are found to be contributing to the T_1 process in the frequency range 4 to 30 MHz in 4O.6, and their relative weightages are calculated as a function of temperature. While ODF is found to be mediating the relaxation at low frequencies (< 10 MHz), diffusion is effect in the

entire frequency range in nematic and S_A phases. This is qualitatively different from what is found in a related liquid crystal 4O.8. The reorientations in the temperature range studied are fast and provide a constant background in the dispersion study. The T_1 process in the S_B phase is primarily characterized by reorientational motions, and the slowing down of diffusion on the onset of the S_B phase is evident both from the T_1 and the T_{1D} data. The estimates of the diffusion coefficients and of activation energies of different molecular processes in the various mesophases quantify the above picture of molecular dynamics.

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