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Study of Line Shape and Angular Variation of ESR Spectra in Two Smectic A Liquid Crystals

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Electron spin-resonance (ESR) measurement of the androstane nitroxide spin-probe is reported in isotropic, nematic and smectic A phases of the liquid crystals *N*-(*p*-Octyloxy-benzylidene)-*p*-toluidine [OBT] and *p*-nitrophenyl-*p*-*n*-octyloxy benzoate [NPOB]. Mono-domain samples in flat quartz tube were formed for the study of the angular variation of the spectra in smectic A phase. The analysis of the spectra using the theory of Polnaszek, Bruno and Freed (PBF) has resulted in the determination of the order parameter S , the rotational correlation time τ_R , and the anisotropic diffusion parameter N at different temperatures. The comparison between the two samples shows that the molecular geometry of the liquid crystals play important role in determining the value of the order parameter. The entire smectic A phase in OBT is characteristic of slow tumbling region ($\tau_R > 10^{-9}$ sec) and the anisotropic parameter N shows an anomalous increase in this phase. This indicates that the slowly relaxing local structure (SRLS) mechanism plays important role in the slow tumbling region. In NPOB the incipient slow tumbling region is almost at the end of smectic A phase and the SRLS mechanism does not seem to play as important role as in OBT.

1. INTRODUCTION

The ESR spectra of liquid crystals in smectic A phase have the simplicity of the spectra in the nematic liquid crystals in the sense that both show uniaxial characteristic¹ and are free from the complexity of tilt angle found in the spectra of other smectic mesophases.² At the same time, because of increased ordering in smectic A, the spectra in this phase is

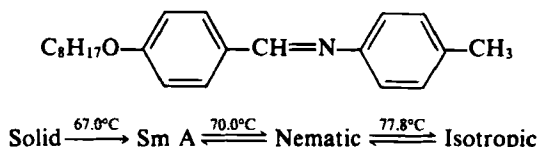
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expected to present increased slow tumbling features of the probe. In the present paper we have made ESR study of two liquid crystals, which have both nematic and smectic A mesophases. The spectra is analyzed using PBF theory,³ which is valid for both motional narrowing and slow tumbling region. The present work therefore is an extension of our recent ESR study⁴ where the liquid crystals showing only nematic mesophase were investigated.

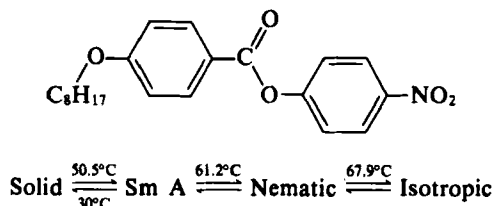
2. EXPERIMENTAL

The two liquid crystals used in the present investigation and their transition temperatures are as follows:

(i) *N*-(*p*-Octyloxybenzylidene)-*p*-toluidine (OBT)^{5,6}



(ii) *p*-nitrophenyl-*p*-*n*-Octyloxybenzoate (NPOB)^{7,8}



The OBT sample was purchased from M/s. E. Merck (England) while NPOB was acquired by Dr. B. Bahadur of this laboratory from Prof. Demus of Martin Luther University, G.D.R.

Since both these liquid crystals are diamagnetic it is essential for ESR study to dope them with some paramagnetic probe. The nitroxide androstane probe used earlier⁴ is found suitable for the present investigation also. Samples with probe concentration of less than 0.1% was taken in a flat quartz tube. The two parallel flat walls, being very close together with separation ≈ 1 mm, can be considered as nearly equivalent to two parallel glass plates. The nematic mesophase is obtained by placing the sample inside the spectrometer cavity and cooling it from isotropic phase in presence of working magnetic field (3.3 KG) acting

perpendicular to the flat faces of the tube. This aligns the director parallel to the magnetic field. The field was then increased to 10 KG and the temperature was slowly lowered till Sm A phase was formed. The N-Sm A transition was cycled this way few times in presence of high magnetic field. This fixes the Sm A director perpendicular to the flat face of the tube and remains so even when the tube is rotated in the working magnetic field (≈ 3.3 KG) for the study of angular variation of the spectra in Sm A phase (however, see section 4.2). The ESR measurements were carried out in the temperature range 45°C – 85°C by using Varian V-4502 X-band (9.3 GHz/sec) ESR spectrometer, 100 KHz magnetic field modulation and Varian V-4547 variable temperature accessory. The ESR spectra were recorded (Figures 1 and 2) in cooling cycle for both the samples.

3. THEORETICAL CONSIDERATIONS

The spin-Hamiltonian for an androstane nitroxide probe, with isotropic g -tensor and axial hyperfine tensor,⁹ can be written as^{10,11}

$$\mathcal{H} = g\beta B \cdot S + aS \cdot I + \sum_{q,q'} A_{2,q}^0 D_{q,0}^2(\Omega) D_{q,q'}^2(\Omega_B) T_2^q \quad (1)$$

where a is isotropic hyperfine parameter equal to $(a_{\parallel} + 2a_{\perp})/3$, while a_{\parallel} and a_{\perp} are parallel and perpendicular components respectively of hy-

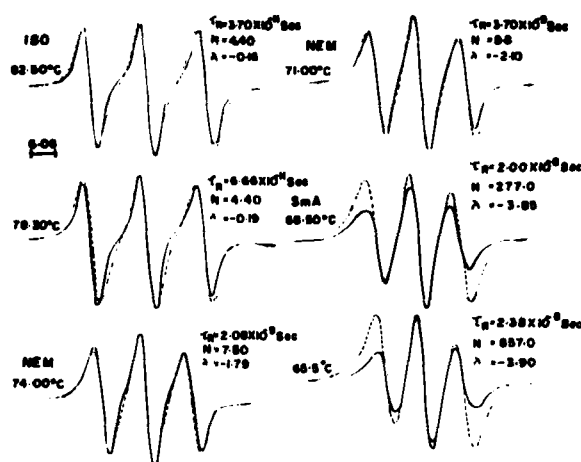


FIGURE 1 ESR line shape simulations for the liquid crystal OBT using PBF theory. ----- Theoretical, ——— Experimental.

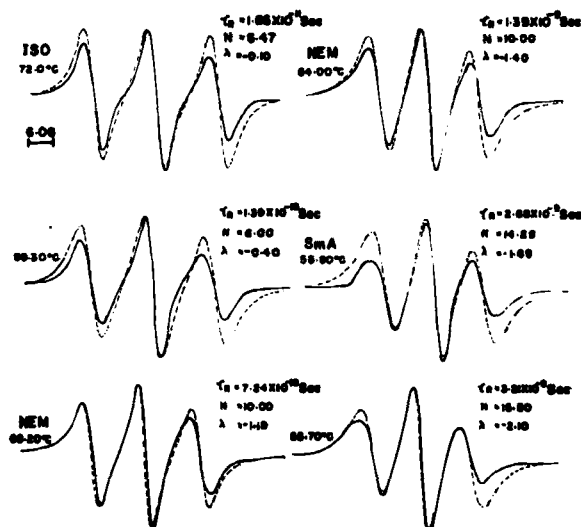


FIGURE 2 ESR line shape simulations for the liquid crystal NPOB using PBF theory. ----- Theoretical, ——— Experimental.

perfine tensor referred to the molecular axis (N—O bond) of the probe. Ω and Ω_B are Eulerian angles specifying the orientations of the probe molecule and the magnetic field B with respect to the director axis of the liquid crystal. $D_{K,M}^L$ are Wigner rotational matrices and

$$\begin{aligned}
 A_2^0 &= \sqrt{\frac{2}{3}} (a_{\parallel} - a_{\perp}) \\
 T_2^0 &= \sqrt{\frac{2}{3}} \left[I_z S_z - \frac{1}{4} (I_- S_+ + I_+ S_-) \right] \\
 T_2^{\pm 1} &= \mp \frac{1}{2} [I_+ S_z + I_z S_{\pm}]; \quad T_2^{\pm 2} = \frac{1}{2} (I_+ S_{\pm})
 \end{aligned} \quad (2)$$

For fast tumbling the dynamical Hamiltonian \mathcal{H} can be replaced by a pseudo-static spin-Hamiltonian.

$$\mathcal{H} = \langle \mathcal{H} \rangle = g\beta B \cdot S + aS \cdot I + \sum_q SA_2^0 D_{q,0}^2(\Omega_B) T_2^q \quad (3)$$

Where $S = \langle D_{00}^2(\Omega) \rangle$ is the order parameter. \mathcal{H} is equivalent to a spin-Hamiltonian of a paramagnetic center with axial hyperfine components given by^{10,11}

$$\tilde{a}_{\parallel} = SA_2^0 + a, \quad \tilde{a}_{\perp} = -\frac{1}{2} SA_2^0 + a \quad (4)$$

To first order in hyperfine interaction the spacing between the adjacent hyperfine components in ESR spectrum is given by¹²

$$\langle a(\alpha) \rangle = \{\tilde{a}_1^2 + (\tilde{a}_\parallel^2 - \tilde{a}_1^2) \cos^2 \alpha\}^{1/2} \quad (5)$$

Here α is the angle between the magnetic field and the director. Eq. (5) gives angular variation of $\langle a \rangle$ in the smectic A Phase. In the nematic phase, since the magnetic field and the director axis always point in the same direction, $\langle a \rangle$ shows no angular variation.

Equation (4) is derived on the assumption of fast tumbling and is not expected to give correct value of the order parameter for slow tumbling region (rotational correlation time $\tau_R > 10^{-9}$ sec). The correct value of the order parameter S is calculated using the following expression

$$S = \langle D_{00}^2(\theta) \rangle = \int_0^\pi d\theta \sin \theta \frac{1}{2} (3 \cos^2 \theta - 1) P_0(\theta)$$

$$P_0(\theta) = \exp(\lambda \cos^2 \theta) / \int_0^\pi d\theta \sin \theta \exp(\lambda \cos^2 \theta) \quad (6)$$

$$\lambda = -\epsilon/kT$$

The value of λ at different temperatures is decided by the best simulation of the spectra using PBF theory³ and one term Maier-Saupe potential $U = \epsilon \cos^2 \theta$, where θ is the angle between the N—O bond direction of the probe and the director. The equations utilized for the simulation are those appropriate for anisotropic viscosity rotational diffusion and are given in Ref. 4. The computations are done for $\alpha = 0$ only, that is for the situation when the magnetic field and the director point in the same direction.

4. RESULTS AND DISCUSSION

4.1 Order parameter

The order parameter S for the two liquid crystals calculated using Eq. (6) are compared in Figure 3. S is zero in the isotropic phase where the probe molecules are oriented at random and $\langle 3 \cos^2 \theta \rangle = 1$. The order would be maximum if the long axis of the probe is completely aligned to the director, that is when the probe molecular axis (N—O bond direction⁴) is perpendicular to the director. This corresponds to $\theta = \pi/2$ or $S = -0.5$. The order parameter S , therefore, lies between 0 and -0.5 . Its magnitude increases with decrease in temperature in the nematic phase of both the liquid crystals. $|S|$ increases with decreasing temperature in smectic A phase also, though the temperature depend-

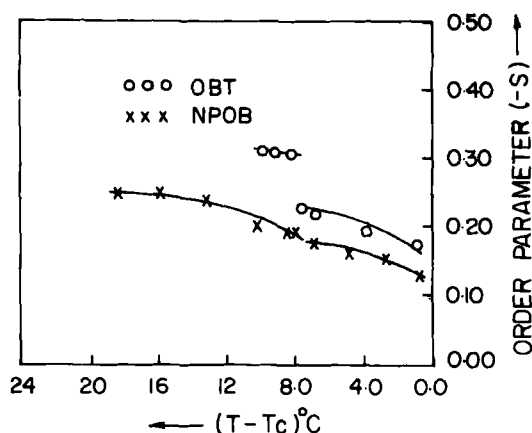


FIGURE 3 Temperature variation of order parameter.

ence is less than that in nematic phase. Sudden jump (Figure 3) in the value of S for OBT at nematic-smectic A transition temperature supports the first order nature of this transition.¹³ The curve for NPOB shows only a little break and indicates that the phase change in this case is a weak first order or second order.

The nematic range in NPOB is about 10°C below the nematic range in OBT. Also the smectic-solid transition temperature in NPOB is about 17°C below the corresponding temperature in OBT. The temperature consideration alone would, therefore, suggest higher ordering in NPOB compared to OBT, since the lower temperature implies lesser thermal agitation and better ordering. This is opposite to the result in Figure 3, which shows that the order parameter for OBT is higher than that for NPOB. This is due to the difference in the molecular geometry of the two liquid crystals. The effect of ester linkage in NPOB is to make its molecules less axial compared to the linear chain molecules of OBT. The liquid crystal OBT therefore has greater tendency, compared to NPOB, to arrange their molecules with their long axes parallel to each other. It must be mentioned here that the order parameter measured by ESR is the orientational order of the spin-probe as influenced by the orientation of the director and therefore the observed order is very dependent upon the length and shape of the probe. The probe order parameter, however, is expected to follow the same functional form as the liquid crystal order provided that the molecular length of the two are comparable.

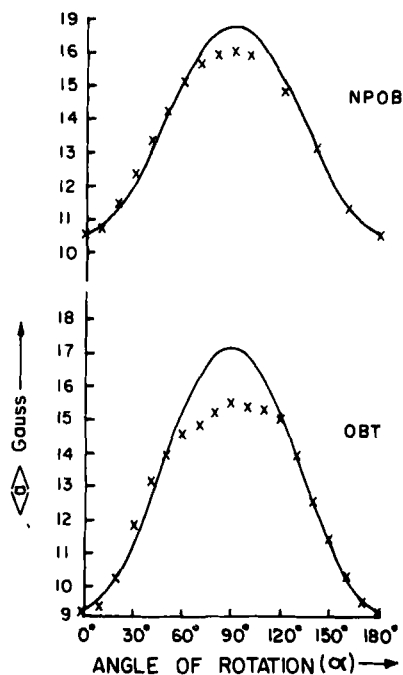


FIGURE 4 Angular variation of hyperfine separation $\langle a \rangle$. XXX are experimental points.

4.2 Angular variation in smectic A phase

Figure 4 shows the angular variation of the separation between the adjacent hyperfine components in the spectra of OBT at 68.54°C and NPOB at 56.74°C. Also shown in the figure are the theoretical curves derived from Eqs. (4) and (5) where the values of the order parameter $S = -.310$ for OBT and $S = -.245$ for NPOB are used. These S -values are calculated from Eq. (6) using the λ -values required to give the best simulation of the spectra for $\alpha = 0$, that is when the magnetic field and the director point in the same direction. The theoretical curves compare well with the experimental results except near $\alpha = \pi/2$, where the experimental points are slightly below the corresponding theoretical curves. This difference between the two sets of results indicates that the Sm A is not completely aligned as a monodomain. The angular variation of the spectra does, however, show that by following the procedure for a glass plate sample¹⁴ a reasonable monodomain sample can be

formed in a flat glass tube also, though the small curved surface of the flat tube will have the tendency to disturb this alignment. It is expected that this curved surface effect can be overcome and a better aligned sample can be made if the N-Sm A transition is cycled in a higher magnetic field than that presently available at our disposal (≈ 10 KG).

4.3 Diffusion parameter and correlation time

The computer simulated ESR spectra based on PBF theory are compared in Figures 1 and 2 with the experimental spectra of the two liquid crystals at different temperatures. The effect of the anisotropic viscosity rotational diffusion are presented in these figures in terms of the ordering parameter λ , the anisotropic parameter $N = R_{\parallel}/R_{\perp}$, and the rotational correlation time $\tau_R = (1/6)R_{\perp} \cdot R_{\parallel}$ and R_{\perp} and R_{\parallel} are the components of rotational diffusion tensor \mathbf{R} parallel and perpendicular to the director axis respectively. The curves τ_R versus $1/T$ show Arrhenius plots in isotropic, nematic and smectic A mesophases of both the liquid crystals (Figure 5). The rotational correlation time τ_R in OBT is $\approx 10^{-10}$ sec in isotropic, $\approx 10^{-9}$ sec in nematic and $\approx 10^{-8}$ sec in smectic A mesophase. In NPOB the values are $\approx 10^{-11}$ sec in isotropic phase and $\approx 10^{-9}$ sec in nematic and smectic A mesophases. The activation energies for OBT are 15.14 kcal/mole in nematic and 8.58 kcal/mole in smectic A mesophase. The corresponding values for NPOB are 13.32 kcal/mole and 6.93 kcal/mole respectively. These are typical values for the liquid crystals in these mesophases.^{4,11,15,16}

The value of N in isotropic phase is ≈ 6 in NPOB and ≈ 4.5 in OBT. These values are close to the probe value⁴ of ≈ 5 . The decrease in temperature reduces the rotational motion and the effect of ordering is to cause preferentially more quenching of rotation along an axis perpendicular to the director than along the director itself. As a result N increases in the nematic phase. Larger increase in N in OBT from ≈ 4.5 to ≈ 9 compared to that in NPOB from ≈ 6 to ≈ 10 is expected in view of the higher ordering in OBT. In the smectic A phase in OBT R_{\parallel} shows appreciable increase (Figure 6) while R_{\perp} has normal decreasing trend with decreasing temperature (Figure 5). This results in an appreciable increase in N . It should be noted that the entire smectic A phase of OBT is the region of the characteristic slow tumbling of the probe ($\tau_R > 10^{-9}$). In earlier studies^{4,11,14,15} the increase in R_{\parallel} with decreasing temperature in the incipient slow tumbling region is ascribed to the fact that the instantaneous potential on the probe is not just the mean time averaged potential U . Instead an additional instantaneous fluctuating potential $U'(t)$ with zero mean, $\langle U'(t) \rangle = 0$, is also present.

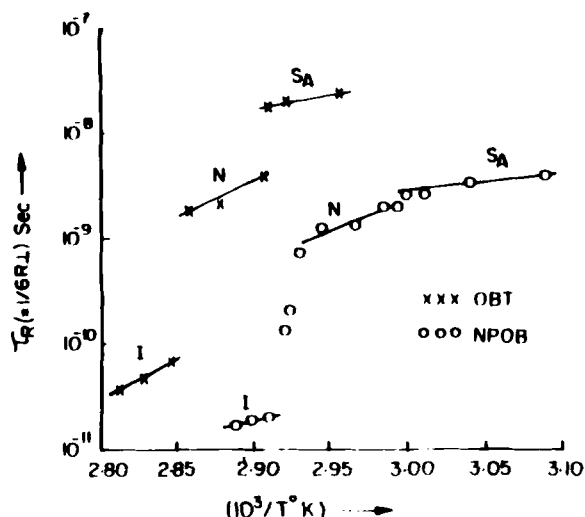


FIGURE 5 Temperature variation of rotational correlation time τ_R (sec/rad) in logarithmic scale.

The origin of this additional potential is the coupling between the probe modes and the localized modes of the surrounding solvent molecules. The fluctuating torque due to $U'(t)$ presents a local structure on the probe molecule, which relaxes on a time scale much slower than the reorientation of the probe molecule. This slowly relaxing local structure (SRLS) mechanism is responsible for the apparent large increase of the anisotropy in the diffusion tensor.^{14,15} In NPOB the incipient slow tumbling region is at much lower temperature, that is almost at the end of the smectic A phase (Figure 2). R_{\parallel} in this case shows only marginal increase (Figure 6) with decrease in temperature and the SRLS mechanism does not seem to play as important role as in OBT.

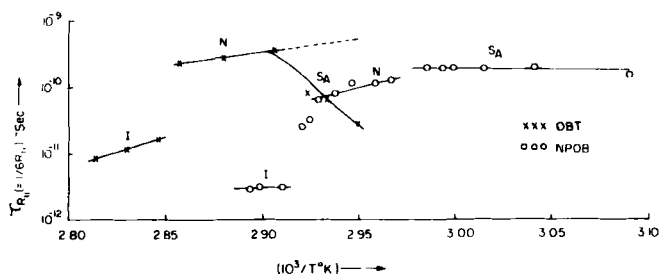


FIGURE 6 Temperature variation of rotational diffusion tensor component R_{\parallel} (sec⁻¹).

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