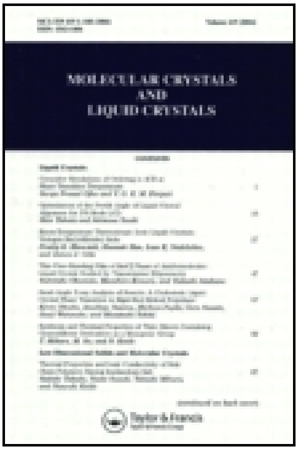

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EPR Study of a Nematic Liquid Crystal near the Isotropic-Nematic Phase Transition

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The temperature dependence of the hyperfine splitting and widths of the absorption lines of the system HOAB + VACA is studied using the EPR technique. Special attention is devoted to the changes of the hyperfine splitting and linewidths in the vicinity of the isotropic-nematic phase transition.

INTRODUCTION

Many EPR studies of paramagnetic probes dissolved in liquid crystals have been performed. From the change of the hyperfine splitting as a function of the temperature certain information about the orientational order of the liquid crystal molecules can be obtained.[1-3] Experiments show, in general, that liquid crystals do not align all paramagnetic probes equally well. The degree of the orientation (the order parameter) depends strongly on the paramagnetic probe molecular geometry, size and rigidity. The order parameter is defined by

$$\mathcal{S} = \frac{1}{2}\overline{(3\cos^2\beta - 1)} \tag{1}$$

Where the bar denotes an ensemble average. β is an angle between the long molecular axis and the preferred direction (= direction of the external magnetic field if low viscosity nematic liquid crystals are used). The above definition is valid if the molecules for which the orientational order is studied possess axial symmetry. Although an EPR experiment does not give the order parameter of the liquid crystals directly because the liquid crystal molecules are not paramagnetic, it does give one the degree of ordering of the paramagnetic probes from which conclusions can be inferred regarding the ordering of the liquid crystal molecules themselves.

The EPR signal linewidths of a paramagnetic probe dissolved in an isotropic liquid depend on the dynamics of the solute molecules and hence also on the dynamics of the solvent molecules. Studies of EPR linewidths of paramagnetic probes dissolved in isotropic solvents have been performed.[4-6] Similar studies of the linewidths of paramagnetic probes dissolved in liquid crystals have been reported.[7-9] In these reports it is shown that the expression which describes the linewidth dependence on the molecular quantum number "m_I" has the same form regardless of whether the paramagnetic probe is dissolved in an isotropic or in an anisotropic liquid. The expression describing linewidths of paramagnetic probes dissolved in low viscosity liquids has the form:

$$\Delta H(m_I) = A + Bm_I + Cm_I^2 + Dm_I^3 + Em_I^4 \qquad (2)$$

The parameters A, B, C, D, and E differ if the studied paramagnetic probe is dissolved in an anisotropic liquid from those when a paramagnetic probe is dissolved in an isotropic liquid. The main difference stems from the structures of an anisotropic liquid (ordered) and of an isotropic liquid (disordered).

In this study we report a study of the hyperfine splitting and linewidths of a paramagnetic probe dissolved in a nematic liquid crystal.

Several publications appeared in the recent years where certain pretransitional phenomena have been reported.[10-14] It seemed therefore worthwhile to study the hyperfine splitting and the linewidths of a paramagnetic probe dissolved in a nematic liquid crystal very close to its isotropic-nematic (I-N) phase transition temperature.

EXPERIMENTAL

In our studies we used several nematic liquid crystals and several paramagnetic probes. In this work, we will describe our results only for the system HOAB + VACA (4,4'-di-n-heptoxyazoxy-benzene + vanadylacetylacetonate). Both, HOAB and VACA were obtained commercially. HOAB was used without further purification, VACA was re-crystalized from acetone. The concentration of the paramagnetic probe was always smaller than 10^{-3} mole. VACA was chosen since it is relatively stable when dissolved in HOAB and since it reflects the order parameter of nematic liquid crystal very satisfactorily.

HOAB has two liquid crystal phases. In the temperature range between 122°C and 92°C it forms the nematic phase and below 92°C but above 74°C it forms the smectic C phase. HOAB was chosen for our measurements because of its low viscosity. Thus the system HOAB + VACA gives a well resolved spectrum. The addition of 10^{-3} mole of VACA to HOAB lowers the I-N temperature about 2°C.

The EPR measurements were obtained with a single crystal detection x-band spectrometer ($\nu = 9160$ MHz using 100 KHz field modulation).

The temperature of the cavity (sample) was measured with a Fenwall Electronic Inc. thermistor (GA 51P1), incorporated in a simple bridge. For the measurements very close to the phase transition temperature a special cavity (made of copper) and heating system were constructed. With this apparatus the temperature could be controlled to within 5 millidegrees over a two hour period.

The heating system was composed of a copper sleeve about which a bifilar heating coil was wound. A second thermistor was built into the copper sleeve. This served as the variable feedback resistance and was a part of a Wheatstone bridge. The cavity was mounted in the middle of the copper sleeve and both were inserted into a glass dewar for good heat insulation. The dewar vessel was properly closed to prevent air circulation. In order to change the sample temperature 0.1°C the system required 30 minutes to equilibrate. The relative temperature measurements were accurate to at least 0.01°C, and the absolute temperature was determined to ±1°C. We believe that the temperature gradients which existed across our samples (Length ~ 0.8 cm) were smaller than 0.01°C.

The average volume of the sample studied was ~ 0.5 cm^3. VACA was dissolved in HOAB about 10°C below the I-N phase transition. The samples were inserted into teflon holders. The EPR spectra were recorded under normal atmospheric pressure.

The Hyperfine Splitting

Measurements of the hyperfine splitting of the VACA dissolved in the HOAB as a function of the temperature have been performed[15, 16] In these measurements. however, no attention was given to the changes of the hvperfine splitting and of the linewidths of the absorption lines very close to the I-N phase transition temperature.

For the axially symmetric g- and hyperfine tensor the spin Hamiltonian may be writted as (G.E. Pake 1962).

$$\mathcal{H} = \beta_e [g_{\parallel} H_r S_r + g_{\perp} (H_p S_p + H_q S_q)] + A_{\parallel} I_r S_r + A_{\perp} (I_p S_p + I_q S_q) \quad (3)$$

where $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$, $A_{\perp}$ are the parallel and perpendicular components of the g- and hyperfine tensors, respectively. It has been shown[18] that a choice of the proper coordinate system leads to the following spin Hamiltonian for the axially symmetric paramagnetic probes dissolved in nematic liquid crystals:

$$\mathcal{H} = g\beta_e H_z S_z + aI \cdot S + \frac{1}{3}(\Delta g\beta_e H_z + bI_z)\,\overline{(3\cos^2\beta - 1)}\,S_z \quad (4)$$

When Δg is zero the separation between two lines corresponding to $\pm m_I$ is

$$2a'm_I = 2am_I + \frac{2}{3}b\,\overline{(3\cos^2\beta - 1)}\,m_I$$

Here a′ is the experimentally measured hyperfine splitting (distance between the first and last lines divided by seven for VACA) and for an isotropic solution $a' = a$, where $a = 1/3\,(A_\parallel + 2A_\perp)$ and $b = A_\parallel - A_\perp$.

Measurements were performed both in the isotropic and the nematic phases. The hyperfine splitting changes considerably when lowering the temperature from the isotropic to the nematic phase (Figure 1). The order parameter calculated from these measurements is consistent with NMR.[19] and optical measurements. This indicates that the VACA molecule reflects the molecular organization of HOAB fairly well. From the magnitude of hyperfine splitting it is possible to conclude that the symmetry axis of the hyperfine interaction of the VACA dissolved in the HOAB nematic phase is aligned perpendicular to the external magnetic field implying that the long VACA molecular axes are (partially) aligned parallel to the liquid crystal long molecular axis. The I-N phase transition temperature is taken as that temparature where the slope of the hyperfine splitting versus temperature is the steepest (T_c = 119.45°C for the system HOAB + VACA).

From Figure 1 one can see that the hyperfine splitting of VACA does not change abruptly at the I-N phase transition.

Thus assuming that VACA shows the true order parameter at the I-N phase transition temperature, then our experiments show that the ordering of the

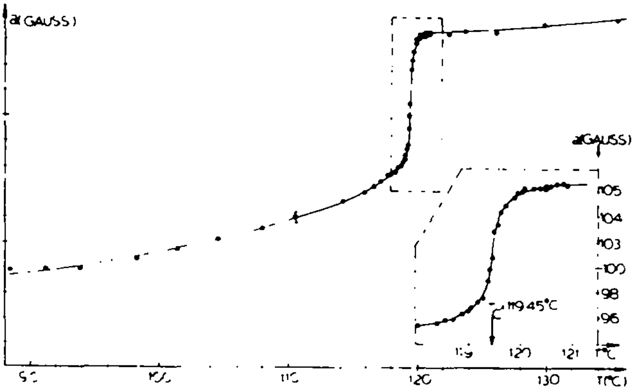

FIGURE 1 The hyperfine splitting of the VACA dissolved in HOAB as a function of the temperature. The hyperfine splitting does not change sharply at the isotropic-nematic phase transition temperature. This can be clearly seen in the enlarged section in the right lower corner of this figure.

liquid crystals molecules starts before the I-N phase transition temperature is reached. Since the interaction of a single liquid crystal molecule with the external magnetic field is too weak to overcome the thermal energy then a large number of molecules must be correlated in the isotropic phase very close to the I-N phase transition temperature.[20] This correlation might be caused by the appearance of elastic constants characteristic for the liquid crystal structures at the I-N phase transition temperature.

The Linewidth

The EPR linewidths of the dissolved paramagnetic probes are dependent on solvent motions. Therefore, the EPR spectrum of a free radical may contain a wealth of information about solvent molecular motions. Clearly, dissolved solute molecules affect the solvent molecular motions. To what extent solvent properties are changed is not understood completely.

One expects that the isotropic phase of a liquid crystal will not differ very much from a normal, low viscosity, isotropic liquid. However, below the I-N phase transition temperature certain reorientational motions become hindered because the molecular motions are not isotropic and this causes characteristic changes in the relaxation time.

In recent years several publications have appeared,[7-9] where the shapes and linewidths of the free radicals dissolved in nematic liquid crystals were discussed. Both, Glarum and Nordio discuss g- tensor and hyperfine interactions and their final equations for the linewidths are identical. The only difference is the description of the molecular motions by a single correlation time[7] and by several correlation times.[8]

Glarum assumed that the correlation function decays exponentially and that the correlation time of the paramagnetic solute is the same as for the solvent molecules which is given by the Debye equation

$$\tau_c = \frac{4}{3}\frac{\pi}{k}\frac{\eta}{T} r^3$$

where "r" is the hydrodynamic radius of the solute molecule, and η is the flow viscosity of the fluid. For the type of the measurements reported here the rotational viscosity coefficient, γ_1, might be more appropriate.[21]

Since the ordering of the VACA molecules by the HOAB molecules is comparable to the ordering of the pure HOAB molecules we decided to study the system HOAB + VACA in detail.

The width of the high magnetic line ($m_I = +7/2$) is very broad and thus a proper measurement of the width of this line was not possible. Hence only the widths of the seven other lines were measured in detail. Results of our measurements in the isotropic and nematic phases are shown in Figure 2a, b.

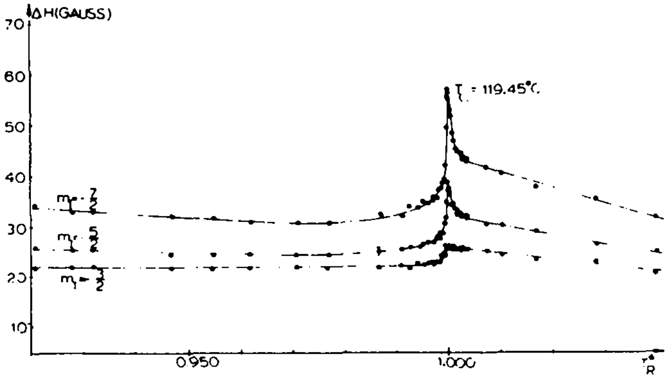

FIGURE 2a The peak to peak linewidths of the system HOAB + VACA as a function of the reduced temperature. The linewidths of the lines for $m_I = -7/2$, $m_I = -5/2$, and $m_I = -3/2$ are shown. The linewidths are maximum at the isotropic-nematic phase transition, $T_R^* = 1.000$.

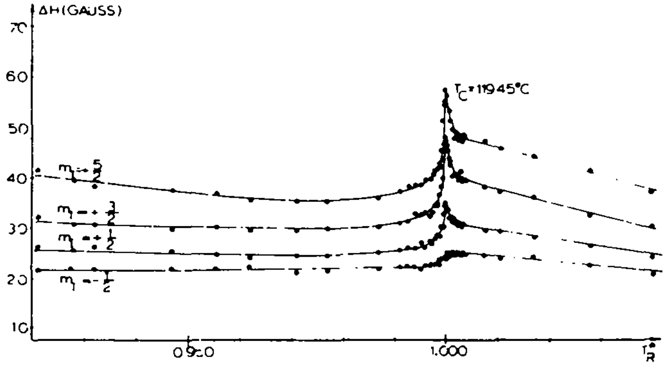

FIGURE 2b The peak to peak linewidths of the system HOAB + VACA as a function of the reduced temperature. The linewidths of the lines for $m_I = -\frac{1}{2}$, $m_I = \frac{1}{2}$, $m_I = 3/2$ and $m_I = 5/2$ are shown. The linewidth of the line for $m_I = 7/2$ is not plotted (see text).

It is clear that the lines in the middle of the VACA spectrum change less than the lines at the ends of the spectrum. This implies either that g-tensor fluctuations do not contribute to the linewidth as much as the fluctuations of the hyperfine tensor or that fluctuations of the g-tensor are smaller than fluctuations of the hyperfine tensor. The hyperfine tensor is however about thirty times more anisotropic than the g-tensor.

In the nematic phase the linewidths decrease. There are two reasons for this decrease of the linewidths in the nematic phase. One reason is that at the phase transition the viscosity of the nematic liquid crystal is lower than the viscosity of the same substance in the isotropic phase at the phase transition. The second reason is the molecular ordering of the liquid crystal, accompanied by a decrease in fluctuations and an alignment of the probe molecules.

Our calculations show that the parameters D and E (Eq. (2)) are very small in the whole temperature range studied except very close to the I-N phase transition temperature. Therefore, we will ignore them in our discussion. The parameters A, B, and C (Eq. (2)) were computed from the data in the Figure 2a, b. A computer program was used to solve the system of seven equations with three unknowns. These parameters which were least square fitted are plotted as a function of the reduced temperature, $T_R^* = \frac{T}{T_C}$, in Figure 3.

It has been shown[22] that the parameter C (isotropic phase) has to be used to calculate the hydrodynamic radius "r" (since the parameter C is not dependent on the spin-rotational relaxation and because it is linear in η/T). The value of the hydrodynamic radius which was calculated from the experimental results of Figure 3 at the reduced temperature $T_R^* = 1.040$ and $\eta/T = 10.6 \times 10^{-5}\ \frac{\text{stokes}}{{}^\circ\text{K}}$ is $r = 3.24 \times 10^{-8}$ cm. This value is consistent with the value obtained from isotropic liquids which do not form liquid crystal phases. In general, the values of the hydrodynamic radius for VACA dissolved in different isotropic liquids[5] are between 3.0 and 3.5Å.

For our calculations in the isotropic and in the nematic phase of the system HOAB + VACA we used Glarum and Marshall expressions for the parameters A, B, and C. The theoretical value of the ratio B/C agrees well with the experimental one over most of the temperature range of the isotropic phase. In Figure 3 we

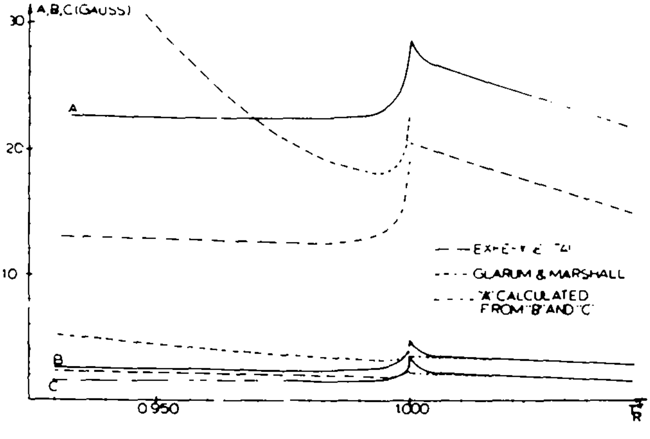

FIGURE 3 The parameters A, B, and C from the equation (2) as a function of the reduced temperature are plotted. The parameters D and E from the same equation are small when compared with A, B, and C. The experimentally obtained parameters in the nematic phase of HOAB do not agree with the calculated ones.

can see that the theoretical curves do not agree with the experimental curves very close to the I-N phase transition.

In the similar way we calculated the theoretical values of the ratio A/C. We find that the theoretical values do not agree with the measured ones. The difference between the measured and calculated A for the isotropic phase of the HOAB is about 7 gauss. Similar disagreements between the theoretical and experimental values A/C have been explained[22, 23] by taking into account the spin-rotational interaction. In our case the spin-rotational contribution to the total linewidths is only 0.3 gauss at $T_R^* = 1.040$ and only about 0.2 gauss at $T_R^* = 1.000$. Therefore, the spin-rotational interaction does not account for the disagreement of the parameter A in our case.

The theoretical expressions for A, B, and C do not take into account effects which take place near the I-N phase transition temperature. Therefore, one is led to a disagreement between the theory and experiment in this temperature region. Our experiments show that very close to the I-N phase transition temperature ($\Delta T < 2°C$) the linewidths increase sharply for all lines except for the lines with $m_I = 3/2$ and $m_I = -\frac{1}{2}$ (Figure 9.2a, b). The maximum linewidth corresponds to the temperature at which the slope of the temperature dependence of the hyperfine splitting is the steepest.

Our studies of the lineshapes of the EPR lines show that close to the I-N phase transition temperature the lineshapes can not be described as at higher temperature, by a simple Lorentzian. The computer fits indicated that the EPR spectrum of the VACA, as one approaches closer than approximately 5°C to T_c, resembles a composite Lorentzian and Gaussian form. This suggests that on the microscale the molecular motions are hindered as if the bulk viscosity were increased. Such an increase of the linewidths, as one approaches the I-N phase transition temperature from above, can be explained by slower collective motions of the liquid crystal molecules.

Glarum and Marshall[7] plotted the linear (B) and quadratic (C) parameter as function of the order parameter. They show that the linear parameter decreases uniformly as the order parameter increases ($S \rightarrow 1.0$) and approaches zero asymptotically. Their study shows that the quadratic parameter C vanishes too, but not in an asymptotic manner. When the order parameter S reaches 0.70 the parameter C is equal zero. With the increasing order parameter it becomes negative and for complete order (S = 1.0) it vanishes again.

Our experimentally determined parameters A, B, and C are shown in Figure 3. The order parameter of the HOAB as obtained from our measurements never reaches 0.7. However, the results plotted in Figure 3 (curves B and C) indicate that parameters B and C start to increase below the reduced temperature $T_R^* = 0.97$ again. At this temperature the order parameter of the HOAB as it is shown by VACA is S = 0.40 (i.e. $\mathcal{O} = -1/2\, S = -0.2$ for VACA since its z-axis is $\perp$ to H).

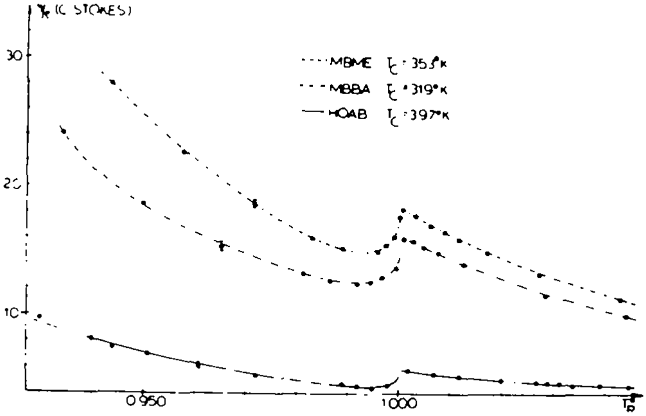

FIGURE 4 The flow viscosities of three nematic liquid crystals are shown. The abbreviations are:

MBME (4-methoxybenzylidene-4-amino-α-methyl cinnamic acid-η-propyl ester)
MBBA (methoxybenzylidene-n-butylaniline)
HOAB (4,4′-di-n-heptoxyazoxybenzene)

We measured the flow viscosity, η, of the pure HOAB (Figure 4). Using Eq. (4) and the order parameter and flow viscosity from our measurements, we calculated the parameters A, B, and C in the nematic phase of HOAB. It is clear that A, B, and C are all in disagreement with our experiment (Figure 3). This is not surprising since the assumption of a single correlation time is surely not valid in liquids such as liquid crystals because of the highly anisotropic intermolecular potential.

We can calculate the parameter A in the nematic phase if we first obtain the needed spectral densities from the measured B and C parameters. Results of such calculations are shown in Figure 3 by the dash-dot curve. The experimental and calculated curve have the same temperature dependence, but the difference in their magnitude is quite significant. The experimental error for the calculated parameter A is large.

Our computer fits have shown that the absorption lines in the nematic phase are slightly asymmetric. As the temperature of the system decreases to the nematic-smectic phase transition lines become more Lorentzian. Similar asymmetry of the VACA absorption lines has been observed previously.[24] and explained in terms of the slow modulation of the orientation of the director. Since this motion is very slow on the EPR scale the observed spectrum is simply a weighted sum of spectra from each possible orientation of the director. This misalignment of the director causes the asymmetry and broadening of the absorption lines and might be partially responsible for the disagreement between the experimental and theoretical value of the linewidth of VACA dissolved in the nematic phase of HOAB.

We had pointed out that according to the Glarum and Marshall's theory parameters B and C should decrease to zero as the order parameter becomes large. Our experiments do not confirm this. The observed increase of these two parameters is probably caused by the increasing viscosity with decreasing temperature (below T = 115°C) in the HOAB nematic phase.

CONCLUSION

From the changes of the hyperfine splitting as a function of the temperature it is possible to conclude that ordering of the liquid crystal molecules starts before the actual phase transition temperature is reached. This was explained by the effects of the external magnetic field on the liquid crystal molecules.

We systematically measured changes of the widths of the absorption lines as a function of the temperature. The absorption lines close to the phase transition temperature do not have the usual Lorentizan shape. The increase of the linewidths at the isotropic-nematic phase transition temperature is explained by the increase of the correlation time of the liquid crystal molecular motions. Changes of the linewidths at T_c indicate that the liquid crystal motions modulate the g-value less than the hyperfine splitting constant.

Our results indicate that a complete study with several different liquid crystals and different paramagnetic probes (possibly at different microwave frequencies) is clearly warranted.

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