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# A Study of the Transient Response of Nematic Phase V to a Redirected Magnetic Field

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The transient response of nematic Phase V to a redirected magnetic field has been explored between 248 K and 272 K by EPR and a new EPR linewidth phenomenon accompanying this transient response has been discovered. The spin probles employed in this work were vanadyl acetylacetonate and 2-(14 carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyloxyl. The transient response for reorientation angles 25° or less leads to an EPR line broadening which relaxes exponentially to the equilibrium value. The relaxation time determined using the vanadyl spin probe at 260 K is 7.3 ± 0.5 sec., and the activation energy for the relaxation process is 14.7 ± 0.4 kcal/mole. Within experimental error there was no dependence of the measured relaxation parameters on the nature of the spin probe employed.

## INTRODUCTION

A number of workers have used EPR to investigate the effect of spinning the mesophase of a nematogen in an applied magnetic field.[1-4] Interpretation of their results through the Leslie equations[5] has involved assuming that there are no macroscopic flows, negligible inertial effects, and uniform director orientation throughout the sample. Luckhurst *et al.* have discussed linewidth effects accompanying sample spinning; however, it is clear that the origins of these effects are not well understood.[3,4] In addition, the effect of temperature on the magnetohydrodynamics of nematics as studied by EPR has yet to be explored.

In a recent paper an EPR study of the ordering and rotational dynamics of vanadyl acetylacetonate (VOAA) in nematic Phase V has been described.[6] Here EPR experiments are reported which describe the transient response of nematic Phase V to changes in the orientation of the applied D.C. magnetic field. This work shows that a linewidth effect accompanies the response of the liquid crystal to the reoriented field, that for small reorientation angles the lineshape relaxes exponentially and that the relaxation process is essentially independent of the spin probe employed in the liquid crystal.

## EXPERIMENTAL

The X-Band EPR spectrometer system and the general sample preparation techniques employed in their study have been described.[6] The nitroxide spin probe 2-(14 carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyl-oxyl (CEDO) was obtained from Syva, and the nematic Phase V from EM Laboratories; both were used without further purification. VOAA was purchased from Alfa Products and was recrystallized from acetone. All experiments were carried out with spin probe concentrations of about $8 \times 10^{-4}\ \overline{M}$ in pyrex tubes with a 2.5 mm I.D. In the studies reported here the transient responses were recorded by:

1) Setting the applied magnetic field at the desired point on the EPR hyperfine line under investigation.

2) Reorientating the magnetic field direction relative to the sample by rotating the magnet the desired angle or in some situations by rotating the sample in the cavity. In general about two seconds were required to reorient the field.

3) Recording the amplitude of the linewidth response on a Hewlett Packard 7004A x-y recorder.

In all situations care was taken to position the sample in the most homogeneous portion of the applied field to avoid field shifts at the sample upon reorientation of the field.

## RESULTS AND DISCUSSION

The results reported here involve a substantial number of measurements in the supercooled region of nematic Phase V. This is simply because the relaxation time at these temperatures is readily measured by our rather crude experimental techniques. It should be noted that previous studies of motion and ordering of VOAA in Phase V have shown that no discontinuities are observed in the EPR spectra or in the subsequent analysis of these spectra when entering the supercooled region. Both the observed isotropic-nematic and observed nematic-solid transition temperatures are clearly discerned by dramatic changes in the EPR spectra.[6] In addition, the work reported here showed no discontinuities in the measured relaxation times in passing to the

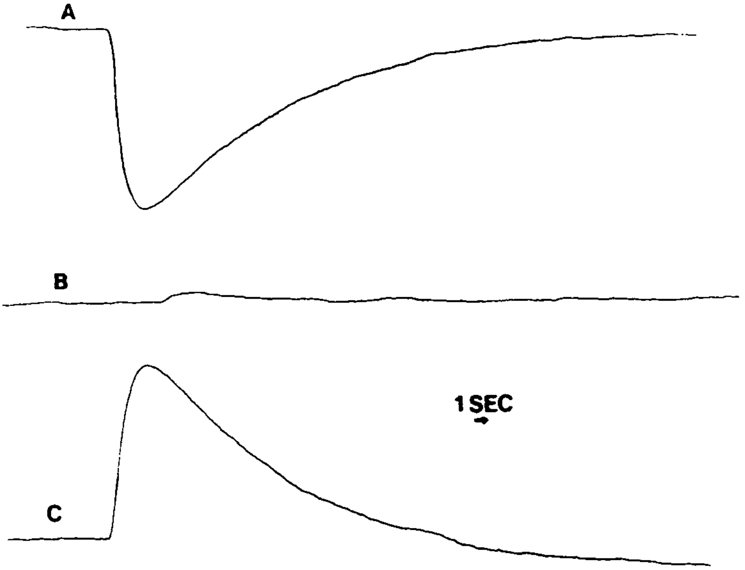

FIGURE 1 Time response of the $\tilde{M} = -3/2$ line for VOAA in Phase V at 260° to a 15° rotation of the magnetic field. *A* shows the response as measured with the magnetic field set at the maximum of the first derivative line, *B* the response with the field set at the zero of the first derivative line, *B* the response with the field set at the zero of the first derivative, and *C* the response with the field set as the minimum of the first derivative. In this figure the initiation of reorientation is reflected by a sharp change in the amplitude of the EPR signal.

supercooled region. Thus, it is assumed that measurements given below reflect the properties of nematic Phase V and are not dependent on supercooling.

The response to reorientation of the magnetic field of the $\tilde{M} = -3/2$ hyperfine line for VOAA in Phase V at 260 K is shown in Figure 1. Here $\tilde{M}$ represents the spectral index number for the hyperfine line in question.[7] The experimental data in Figure 1 was taken with the initial setting of the applied magnetic field at the extrema (*A*,*C*) and zero (*B*) of the first derivative of the EPR absorption. Figure 1 shows that the amplitude of the first derivative signal decreases upon reorientation and that the position of the center of the line is not measurably altered by the reorientation. The data in Figure 1 can be interpreted in terms of Figure 2. In this figure the change in signal amplitude shown in Figure 1 is hypothesized to arise from a broadening of the hyperfine line upon reorientation of the field. Figure 2 shows that shape of the first derivative EPR signal before reorientation (narrow line) and a hypothetical lineshape immediately after reorientation (broad line). In Figure 2 (●) represents the amplitude of the signal at a given magnetic field setting before field reorientation and (▲) the value after field reorientation. The relaxation occurs along the line between the symbols (▲) and (●). In

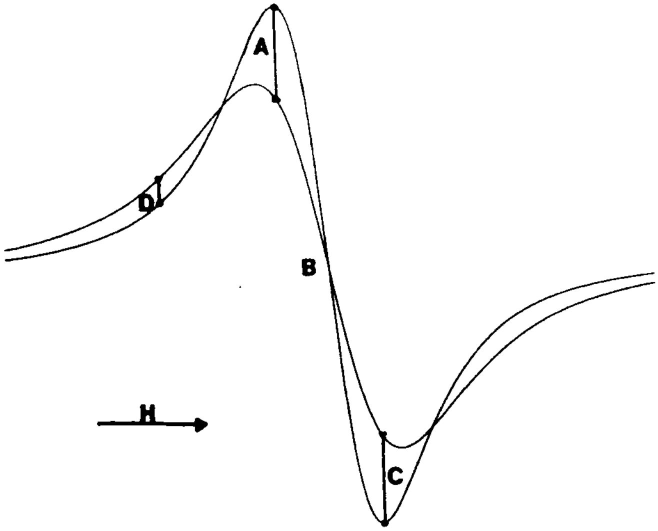

FIGURE 2 Shape of the first derivative EPR signal before reorientation (narrow line) and a hypothetical lineshape immediately after reorientation (broad line). The amplitudes of the EPR signal at a given field setting before field reorientation and after reorientation are represented respectively by the symbols (●) and (▲). The letters *A*, *B*, and *C* identify the spectral regions where curves *A*, *B*, and *C* in Figure 1 were determined.

Figure 2 *A*, *B*, and *C* denote the positions on the first derivative signal at which curves *A*, *B*, and *C* in Figure 1 were determined. The hypothesis that reorientation of the field relative to the sample produces a transient line broadening, can be checked by changing the initial field setting along the first derivative curve from point *A* to point *D*. Experiments, conducted primarily on the CEDO spin probe, have shown that as one moves the setting from *A* toward *D* the amplitude of the reorientation effect decreases in magnitude, disappears, and then reappears with opposite sign. That is the transient response at point *D* has the same shape attributed to *C* in Figure 1. In typical experiments the amplitude of the first derivative EPR signal decreases on the order of 10% for reorientation angles of about 15°.

Analysis of the relaxation curves obtained with VOAA in Phase V between 270 K and 249 K showed that in all cases the relaxation process could be described by the equation:

$$A(t) = A(0)e^{-t}/\tau \qquad (1)$$

Here $A(0)$ is the change in the amplitude of the first derivative signal (in arbitary units) immediately following reorientation of the field, and $A(t)$ is the change in amplitude at some later time $t$. The time characteristic of the relaxation process is represented by $\tau$ in Eq. (1).

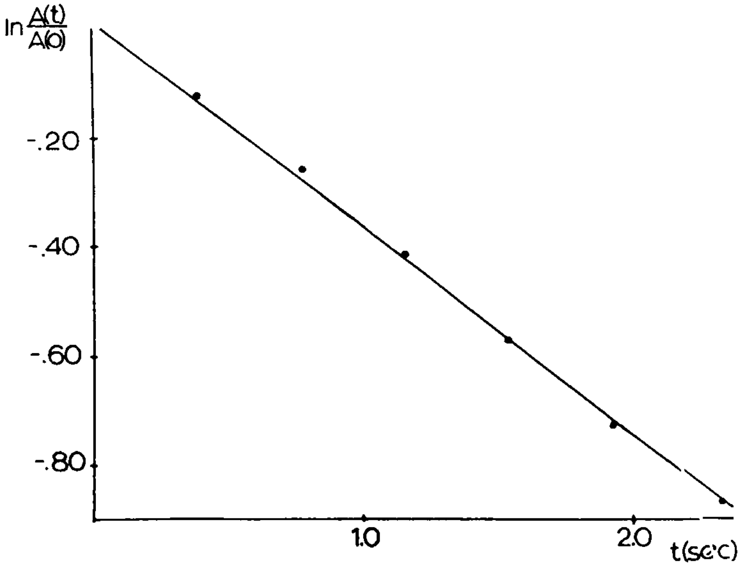

FIGURE 3 A plot of ln $(A(t)/A(0))$ for the $\tilde{M} = -3/2$ line for VOAA in Phase V at 266 K.

Figure 3 shows a plot of $\ln(A(t)/A(0))$ versus $t$ for the $\tilde{M} = -3/2$ line of the VOAA spectrum at 266 K in Phase V. From the slope of the line in Figure 2, a value of 2.5 sec. is determined for $\tau$. It was shown that within experimental error $\tau$ did not depend on the hyperfine line ($\tilde{M}$ value) chosen. For example, at 260 K measurements of $\tau$ for VOAA in Phase V taken from all eight hyperfine lines showed $\tau = 7.3 \pm 0.5$ sec. Here the error represents one standard deviation. A series of measurements on the $\tilde{M} = 1/2$ line at 260 K yielded a value of $\tau = 7.1 \pm 0.2$ sec. while a similar series on the $\tilde{M} = 7/2$ line showed $\tau = 7.4 \pm 0.4$ sec. In all of the experiments carried out with the VOAA spin probe, the field was reoriented by rotating the magnet relative to the sample. No dependence of $\tau$ on the angle of rotation was noted for rotation angles in the range 10°–25°. It should also be noted that all positions on a given EPR absorption curve relaxed with the same $\tau$.

Experiments carried out on Phase V doped with the CEDO spin probe showed that Eq. (1) also described the relaxation process in this system. Figure 4 shows a plot of $\ln(A(t)/A(0))$ for the $\tilde{M} = 0$ line of CEDO in Phase V at 261 K. The value of $\tau$ obtained from the slope of the line in Figure 3 is 5.8 sec. When CEDO is used as the spin probe, the magnitude of $A(0)$ at a given temperature and angle is less than in the case when VOAA is employed as the spin probe. The experiments with CEDO were carried out using both of the techniques described in the experimental section for orientating the

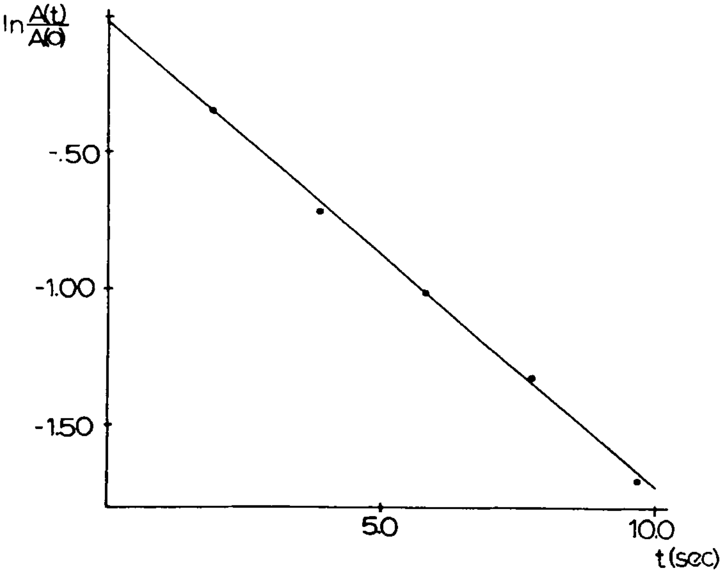

FIGURE 4 A plot of ln $(A(t)/A(0))$ for the $\tilde{M} = 0$ line for CEDO in Phase V at 261 K.

magnetic field direction relative to the sample. No dependence of $\tau$ on the method of field reorientation was noted.

According to the theory of relaxation processes, $\tau^{-1}$ is equal to rate constant which characterized the relaxation process.[8] Figure 5 shows a plot of $\ln(\tau^{-1})$ versus $T^{-1}$ for data obtained using both VOAA and CEDO doped samples of Phase V. Clearly the rate constant for the relaxation process shows an Arrhenius type of temperature dependence. The activation energy determined from a least squares analysis of the VOAA data is 14.7 ± 0.4 kcal/mole while that determined from the CEDO data is 14.8 ± 0.9 kcal/mole.

The above studies do not yield a picture of the complete EPR lineshape during the relaxation process. Presumably this lineshape reflects a distribution in the director for the liquid crystal system.[4] Experiments to determine this lineshape during the transient response and hence the director distribution are planned along with experiments to measure relaxation times shorter than one second.

It is interesting to note that Flanders, using rotating field torque experiments, reported an activation energy of ~9 kcal/mole for the twist viscosity of Phase V, while the activation energy for the process described here is 14.7 kcal/mole.[9] A detailed theoretical analysis of the EPR lineshapes during relaxation would be useful in establishing a relationship between the

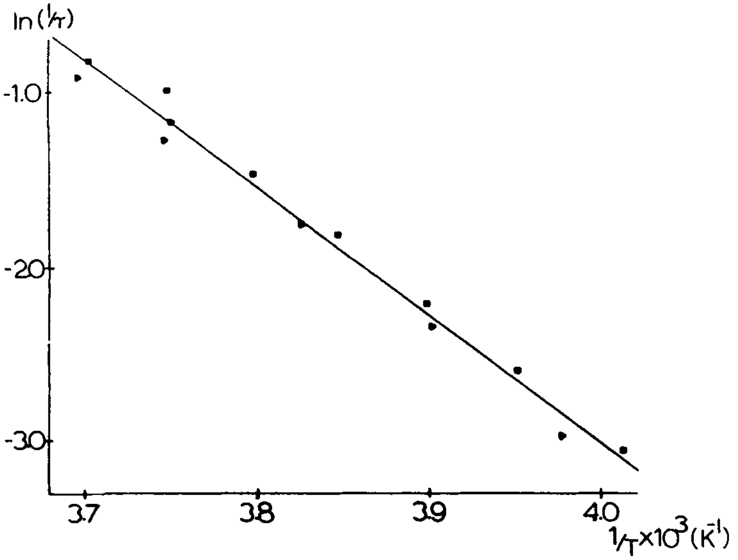

FIGURE 5 A plot of $\tau^{-1}$ versus $T^{-1}$ for (■) VOAA and (▲) CEDO in Phase V.

EPR relaxation experiments described here and techniques designed to measure twist viscosities.

## Note added in proof

More recent studies confirm the results presented here and indicate that above 273 K the relaxation process is characterized by an activation energy of 11 kcal/mole.

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