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C. F. Schwerdtfeger [a] , M. Marušič [a] , A. Mackay [a] & R. Y. Dong [b]

[a] Department of Physics, University of British, Columbia Vancouver, Canada

[b] Department of Statistics, University of Waterloo, Waterloo, Canada

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EPR Study of the Temperature Dependence of Molecular Rotation in Nematic Liquid Crystals†

C. F. SCHWERDTFEGER, M. MARUŠIČ and A. MACKAY

Department of Physics
University of British Columbia
Vancouver, Canada

and

R. Y. DONG

Department of Statistics
University of Waterloo
Waterloo, Canada

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Abstract—The EPR spectrum of vanadyl acetylacetonate dissolved in viscous nematic liquid crystals has been studied as a function of temperature. A plot of the effective order parameter versus temperature shows a definite discontinuity in slope as the molecular rotation passes from weakly to strongly hindered motion. It is shown that viscosity effects do not completely account for this discontinuity in slope. These results are supported by nuclear spin lattice relaxation measurements on the pure liquid crystals which indicate a change in the dominant relaxation mechanism at the same temperature. In slightly less viscous nematics an approximate correction for the viscosity brings the experimental data into fair agreement with a universal curve calculated by Luckhurst.

Introduction

EPR experiments in liquid crystals are made by dissolving a small amount (nominally $\sim 10^{-3}$ M) of paramagnetic material in the liquid crystal and observing the change in the measured value for the hyperfine coupling in going from the isotropic liquid to the nematic phase. Such measurements have been made in nematic liquid crystals as a function of temperature,(1,2) concentration of a second solute(3) and electric field.(4,5) Although several paramagnetic materials have been studied, the most commonly used probe is vanadyl acetylacetonate (VACA). The advantages of VACA are its

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large anisotropic hyperfine tensor, high temperature stability and solubility in many liquid crystals. In this paper we would like to concentrate on the degree of order of VACA in liquid crystals obtained from the measured effective hyperfine coupling and its use in studying the properties of liquid crystals.

Experimental Procedure

The EPR spectra were obtained at 9.1 KMHz using a conventional straight detection system and 100 K Hz field modulation. Field positions were measured to ±0.1 G with a proton magnetometer. The microwave sample cavity was placed in a glass sleeve with a heater coil wrapped around the sleeve and this combination was placed in a glass dewar situated between the magnet pole pieces. The modulation coils were mounted on the stainless steel TE_{102} cavity. The cavity was copper plated to increase the Q value (loaded $Q \sim 4000$). The power dissipated by the 3–10 G modulation employed raised the temperature noticeably and the system required about one half hour to come to equilibrium after the temperature was changed. The temperature measuring thermistor was placed in the sample liquid just outside of the cavity. The thermistors were magnetic but in this arrangement did not affect the large line width spectrum ($\sim$25 G). The temperature could be held constant to within ±0.1 °C and the difference across the sample was less than 0.5 °C. Measurements below room temperature were made with a Varian cavity and an air flow system. Under these conditions the temperature difference across the sample was $\sim$1 °C. The NMR spin lattice relaxation measurements were obtained with a pulse technique which has been previously described.(6)

The liquid crystals were used as obtained without further purification since the nematic-isotropic transition temperatures were in good agreement with the literature values. The mole fraction of vanadyl acetylacetonate in solution was about 10^{-3}. The liquid crystals studied and their measured transition temperatures with and without VACA are given in Table 1. The temperature measurements were made on a Perkin-Elmer DSC-1B direct scanning calorimeter. The viscosity measurements were made with a Fenske capillary tube 300–J781 in a temperature controlled oil bath. Since we are mainly

TABLE 1

Liquid Crystal	Temperature °C Tc (Lit)	 Tc (Meas.)	 Tc (10^{-3}M VACA)
I 4-methoxy benzylidene-4-amino-α-methyl cinnamic acid-*n*-propyl ester	89	83	78
II 4-methoxy benzylidene-*n*-butyl anilene (MBBA)	47	47	44
III 4-methoxy-axobenzene-4-oxy-capronate	106	106	102

interested in relative viscosities we quote in this paper only the kinematic viscosity (η/ρ) in centistokes. The viscosity in centipoise (η) is not very different numerically since the densities of the liquid crystals discussed are close to one.

Results and Discussion

Vanadyl acetylacetonate is a planar molecule whose symmetry is slightly non-axial ($\sim 5\%$). It situates in the liquid crystal with its symmetry axis at right angles to the optic axis. Detailed descriptions of the EPR spectrum expected for VACA in liquid crystals under the extreme conditions of complete motional averaging$^{(1,3,7)}$ and essentially frozen molecules$^{(4,8)}$ have been given. A motionally averaged spectrum consists of eight hyperfine lines whose separation is determined in the isotropic phase by the average hyperfine coupling,

$$a = \tfrac{1}{3}A_{\parallel} + \tfrac{2}{3}A_{\perp}. \tag{1}$$

Here we have taken$^{(4)}$ $A_{\parallel} = -503.4$ MHz and $A_{\perp} = -189.5$ MHz.

In the nematic phase the measured effective coupling constant a is smaller than in the isotropic phase because of the increased order and a degree of order of the system can be defined as$^{(1)}$

$$S \equiv \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle = \tfrac{1}{2}\frac{(\langle a\rangle - a)}{(a - A_{\perp})} \tag{2}$$

When the molecules become very hindered in their motion owing to a large viscosity they can be considered as frozen during the time of a Larmor precession and a " glassy " type spectrum results. In this case the derivative of the absorption spectrum(4) consists of eight slightly asymmetric absorption-like lines whose separation is determined by $A_{\perp}$ and eight smaller peaks whose separation is determined by $A_{\parallel}$. To obtain the order parameter in such a spectrum one must use the relative intensities of the " perpendicular " and " parallel " lines.(4,8)

Most nematic liquid crystals with transition temperatures below 200 °C have viscosities which place them somewhere between these two extremes. We, therefore, have made an estimate of the effect of viscosity on the observed spectra in liquid crystals.

Consider an isotropic liquid as the viscosity is increased, e.g., by cooling, one first observes a normal isotropic spectrum. As the viscosity increases to the point where the molecules become so hindered in their motion that they do not tumble fast compared to the Larmor period ($\sim 10^{-10}$ sec) their spectrum starts to be incompletely averaged. The lines start to broaden and the separation between lines decreases. This continues until the molecules move so slow that they are essentially fixed during a Larmor period. A " glassy " or fixed spectrum then results. That this is indeed the case is demonstrated in Fig. 1 which shows a plot of the measured hyperfine splitting obtained from the total width of the spectrum as a function of the kinematic viscosity for VACA dissolved in

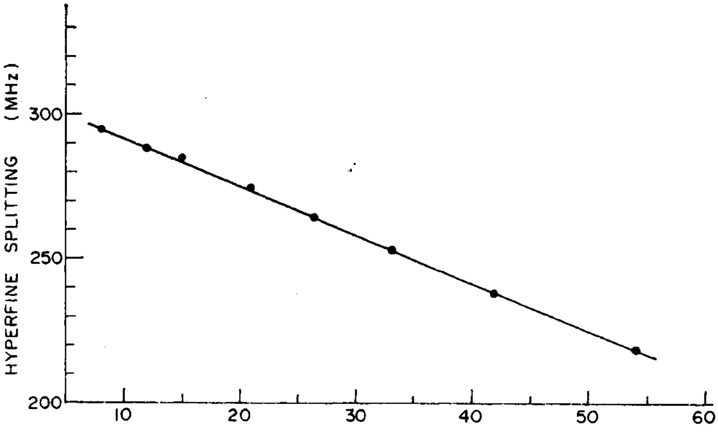

Figure 1. Hyperfine splitting versus kinematic viscosity for 10^{-3}M vanadyl acetylacetonate described in " Octoil " vacuum pump oil.

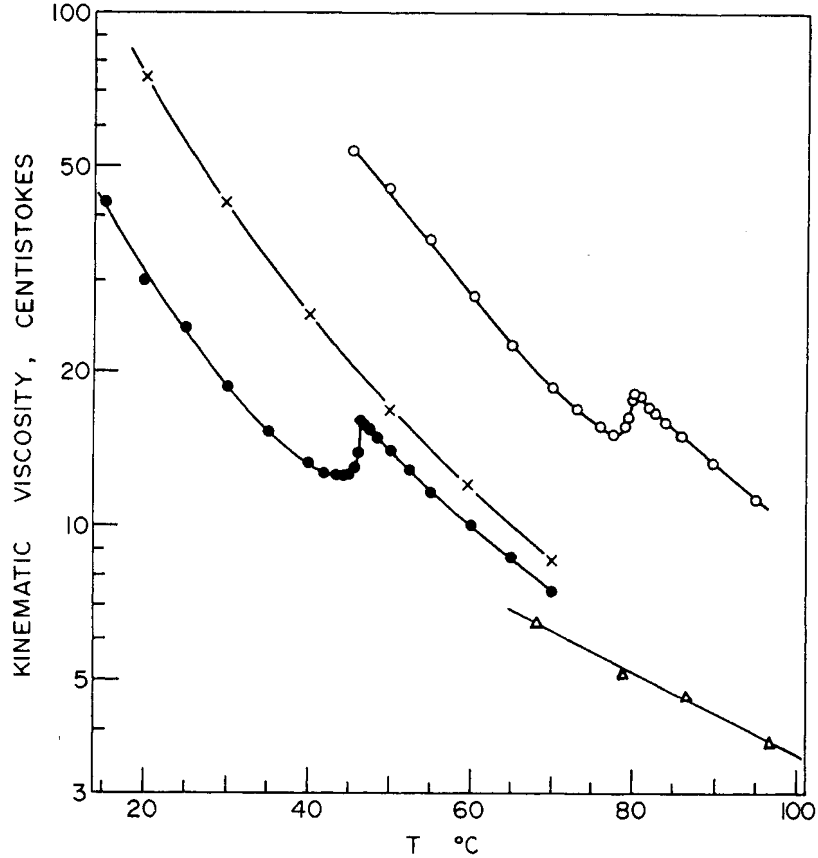

Figure 2. Kinematic viscosity versus temperature for Octoil, ×, and liquid crystals: I, ○; II, ●; III, △ (see Table 1).

" Octoil ",† a vacuum pump oil. This oil was chosen because its viscosity covers the range of the viscosities of the liquid crystals used in this investigation in a similar temperature range. A comparison of these kinematic viscosities is given in Fig. 2. One should note that the measured hyperfine splitting for the VACA in oil already deviates from the isotropic value at a viscosity of ~5 centistokes, therefore, one would expect a similar effect to occur in liquid crystals at comparable viscosities. Figure 3 shows this effect in liquid crystal III (See Table 1). The order parameter has been

† dioctylphthalate.

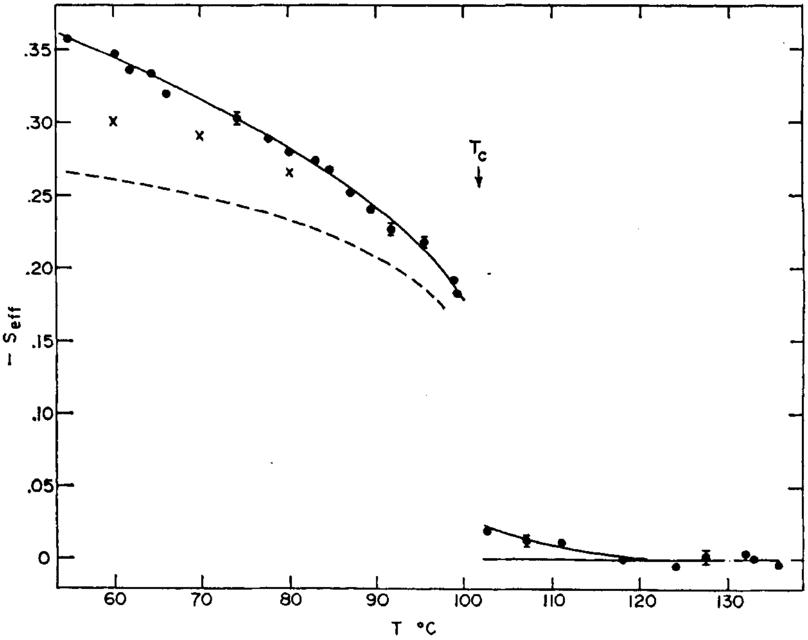

Figure 3. Plot of the effective order parameter versus temperature for Vanadyl acetylacetonate (~10^3M) dissolved in liquid crystal III. The dashed curve is the theoretical curve calculated by Luckhurst (Ref. 2). The points denoted by × are corrections for viscosity as described in the text.

calculated using Eq. (2) but because viscosity also enters we have relabelled it S-effective. We attribute the deviation in the isotropic phase from 120–102 °C to the viscosity. Luckhurst has calculated the theoretical shape of the degree of order versus temperature$^{(2)}$ and compared it to measurements in eight different liquid crystals. We reproduce his theoretical curve as the dashed line in Fig. 3. We have normalized to our data at ~T_c. Our results closely resemble the curves obtained by Luckhurst. In all cases the experimental slope is greater than the theoretical slope. Luckhurst has proposed that a modification of the potential function might produce a better fit. We suggest that a large part, if not all, of the deviation from the theoretical curve can be explained by the effect of viscosity. Qualitatively the effect would be larger at lower temperatures and would give a larger apparent order than that actually present. As a first approximation we have considered that the true order and viscosity effects are additive, $S_{eff} = S_{true} + S_{vis}$. In order to calculate S_{vis} one must use the true average viscosity of the liquid crystal and not the kinematic viscosity. A comparison of viscosity data in other nematic liquid crystals$^{(9)}$ indicates that the average viscosity will approximately continue on slightly lower than the isotropic curve. We have taken it to be parallel to the oil viscosity for our calculation. Normalizing to the liquid crystal data at 99 °C we obtain the points marked × in Fig. 3. These points would be fairly close to a curve parallel to the dashed curve in the figure and show that the viscosity indeed has a large effect on the order parameter determined from the measured hyperfine splitting and could account for the discrepancy in slopes. In order to make a more quantitative conclusion we require the true order parameter of the liquid crystal with the VACA dissolved in it. Optical studies to determine this are in progress in our laboratory.

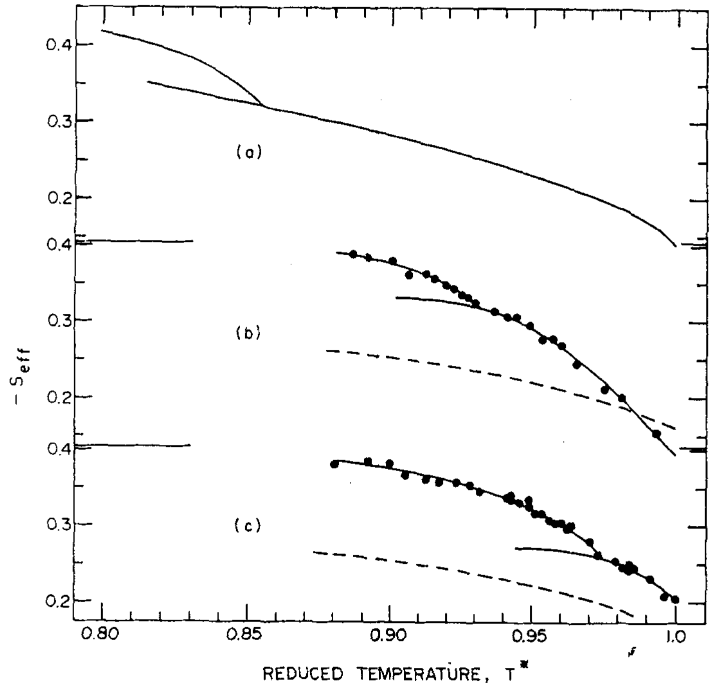

Figure 4. Effective order parameter versus reduced temperature $T^* = T/T_K$, for vanadyl acetylacetonate dissolved in the liquid crystals: (a) bis (4′-n-octyloxybenzal)-2-chloro-1,4-phenylenediamine (Ref. 1), (b) II, and (c) I.

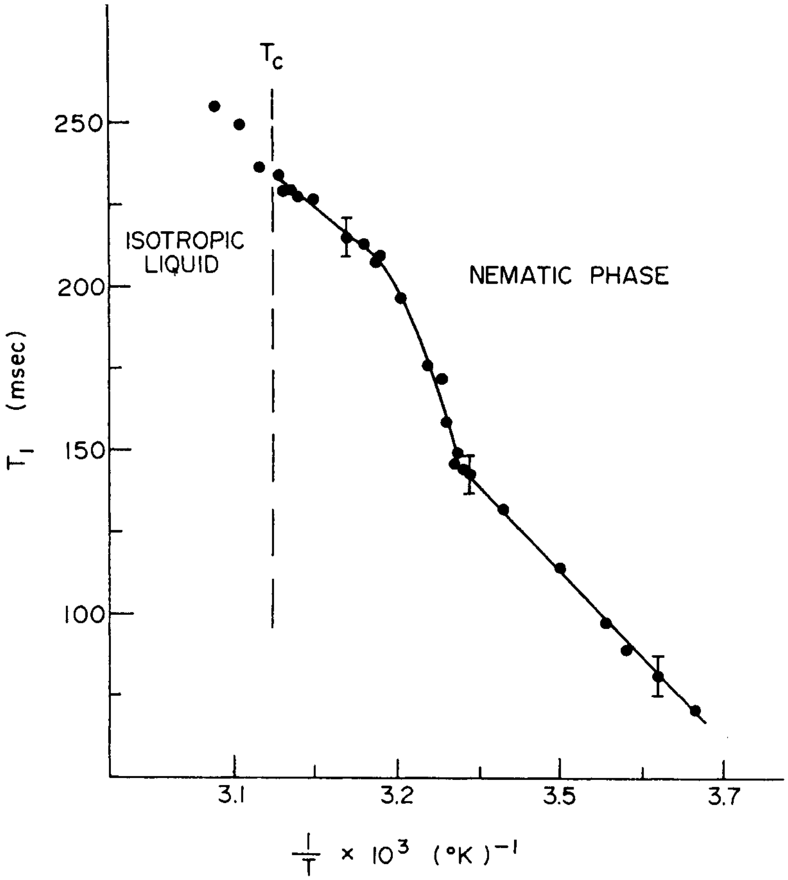

Figure 5. Proton relaxation time T_1 versus reciprocal of the temperature at 18.2 MHz for the liquid crystal II.

As seen in Fig. 2, liquid crystals I and II are very viscous when compared with III. In Fig. 4 is plotted the effective order parameter versus reduced temperature for three viscous liquid crystals. Curve (a) is from recent work by Fryburg and Gelerinter(1) for the liquid crystal bis (4′-*n*-octyloxybenzal-2-chloro-1,4-phenylenediamine). Curves (b) and (c) are liquid crystals II and I of Table 1. The discontinuity in the slope of curve (a) has been ascribed to viscosity effects. Recent NMR spin relaxation (T_1 and $T_{1\rho}$) measurements on liquid crystal I,(10) however, show that there is a change in the dominant mechanism of relaxation at the temperature of the slope discontinuity (~69 °C). We have performed T_1 measurements on the liquid crystal II and found a similar change in the relaxation at

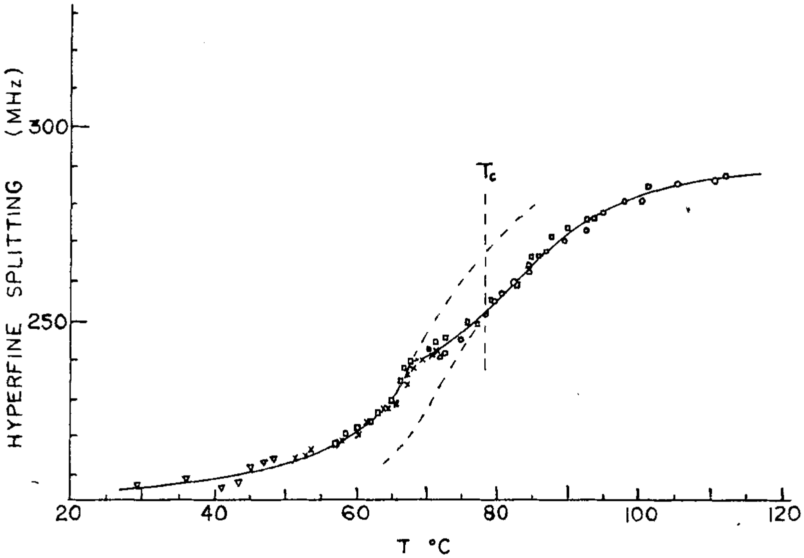

Figure 6. Hyperfine splitting in MHz versus temperature for several samples of vanadyl acetylacetonate (~10^{-3}M) dissolved in liquid crystal I. The dashed curves which represent viscosity effects are discussed in the text.

the temperature of the slope discontinuity (~25 °C). This is shown in Fig. 5. This implies that the liquid crystal is undergoing some physical change. In order to further elucidate this point we have plotted the hyperfine splitting of VACA dissolved in liquid crystal I as a function of temperature in Fig. 6. The dashed curves represent a normalized fit to the viscous oil data. One sees that at T_c the experimental points depart from the normal viscous curve. This is due to a combination of an abrupt decrease in viscosity and an increase in order of the system. As one lowers the temperature further there is a discontinuous change in the slope of the curve. Since both the viscosity and order are smoothly varying functions, it would seem that some other effect must cause the change. This is supported by the NMR T_1 measurements. One possible explanation could be the proposal of Freiser(11) of a uniaxial to biaxial phase transition. Since Haas(12) has recently demonstrated electro-optically that certain liquid crystals including MBBA are biaxial, such a transition is not out of question.

Obviously further experiments which are more sensitive to direction in the liquid crystal than the current NMR and EPR measurements are required before the existence of such a transition can be proven. We feel that the best method of observing this transition would be optically.

In conclusion, we have shown that viscosity effects must be taken into account in interpreting EPR experiments in liquid crystals. We have, in addition, observed a change in the properties of the viscous liquid crystals in their nematic change in both our NMR and EPR results. We suggest that this change may be a uniaxial to biaxial transition.

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