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G. Krüger, H. Spiesecke, R. van Steenwinkel. NUCLEAR MAGNETIC RELAXATION AND SELF DIFFUSION IN SOME LIQUID CRYSTALS SHOWING SMECTIC POLYMORPHISM. Journal de Physique Colloques, 1976, 37 (C3), pp.C3-123-C3-126. 10.1051/jphyscol:1976322 . jpa-00216505

**HAL Id: jpa-00216505**

**<https://hal.science/jpa-00216505>**

Submitted on 4 Feb 2008

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# NUCLEAR MAGNETIC RELAXATION AND SELF DIFFUSION IN SOME LIQUID CRYSTALS SHOWING SMECTIC POLYMORPHISM

G. J. KRÜGER, H. SPIESECKE and R. VAN STEENWINKEL

Magnetic Resonance Laboratory, Physics Division, EURATOM CCR, Ispra, Italy

**Résumé.** — Les temps de relaxation nucléaire,  $T_{1Z}$  et  $T_{1D}$ , et les coefficients de diffusion  $D_{\parallel}$  et  $D_{\perp}$  ont été mesurés en fonction de la température dans éthyl p-(p-éthoxybenzylidène)-amino-cinnamate (EBAC) et dans TBBA. Les résultats montrent que la diffusion contribue aux vitesses de relaxation dans les phases smectiques A, C et H de TBBA et les phases A et B de EBAC.

La diffusion perpendiculairement au directeur est clairement du type *diffusion liquide* dans les phases A et C. Dans la phase B de EBAC, d'autre part, la diffusion se fait par sauts comme dans un pseudoréseau.

**Abstract.** — Nuclear magnetic relaxation times  $T_{1Z}$  and  $T_{1D}$  and the self diffusion coefficients  $D_{\parallel}$  and  $D_{\perp}$  have been measured in dependence of temperature in ethyl p-(p-ethoxybenzylidene)-amino-cinnamate (EBAC) and TBBA. The results show that the diffusion process contributes to the relaxation rates in the smectic A, C and H phases of TBBA and in the smectic A and B phases of EBAC. Evidence is given that the diffusion perpendicular to the molecular director is liquid like in the A and C phases and of a pseudolattice jump type in the B phase of EBAC.

**1. Introduction.** — Recently, we have studied nuclear magnetic relaxation together with both impurity and self diffusion in p-dodecanoylbenzylidene-p'-aminoazobenzene which shows one nematic and various smectic phases [1, 2]. Since these results were not sufficient to clarify the general behaviour of magnetic relaxation and self diffusion in substances showing smectic polymorphism we report here on investigations done in two somewhat different substances of this kind, namely ethyl p - (p - ethoxybenzylidene) - amino cinnamate (EBAC) and terephthal-bis-(p-butylaniline) (TBBA).

The latter is also interesting since we can compare our results with those obtained by NMR at other frequencies [3, 4] and by neutron scattering [5].

**2. Experimental.** — All our experiments were done by first heating the sample to the isotropic range, then cooling it down to the nematic regime where it was allowed to stay for some time in order to get the molecules oriented in the magnetic field. This initial orientation of the molecules in the sample was then kept for all the measurements.

The Zeeman relaxation time  $T_{1Z}$  was measured at 15 MHz in the usual way, the dipolar relaxation time  $T_{1D}$  with a  $90^\circ$ - $\tau$ - $45^\circ_{90^\circ}$ - $\tau$ - $45^\circ$  pulse sequence [7]. In these measurements the temperature of the sample was controlled to better than  $\pm 0.05$  K, and the temperature gradient over the sample was less than  $\pm 0.01$  K. The errors on  $T_{1Z}$  and  $T_{1D}$  are estimated to be  $\pm 5\%$  and  $\pm 10\%$  respectively.

The self diffusion coefficients were measured by two pulse proton spin echo at 48 MHz. In the smectic phases the sample was oriented to the magic angle and the pulsed field gradient of up to 1.2 kOe/cm was applied either parallel or perpendicular with respect to

this direction. Thus the two diffusion coefficients, parallel ( $D_{\parallel}$ ) and perpendicular ( $D_{\perp}$ ) with respect to the orientation of the molecular director could be measured. Our measuring accuracy is typically  $\pm 10\%$  for both  $D_{\parallel}$  and  $D_{\perp}$  in smectic A phases. In the smectic C phase of TBBA we have an approximate error of  $\pm 20\%$  and in the smectic B phase  $\pm 30\%$ . This is due to the shorter value of  $T_2$  in C and B phases even at the magic angle orientation. In this case the temperature was only regulated to  $\pm 0.4$  K and the absolute accuracy was  $\pm 2$  K.

**3. Results.** — **3.1 RELAXATION.** — The results are shown in figures 1 to 4. In the nematic phase of EBAC

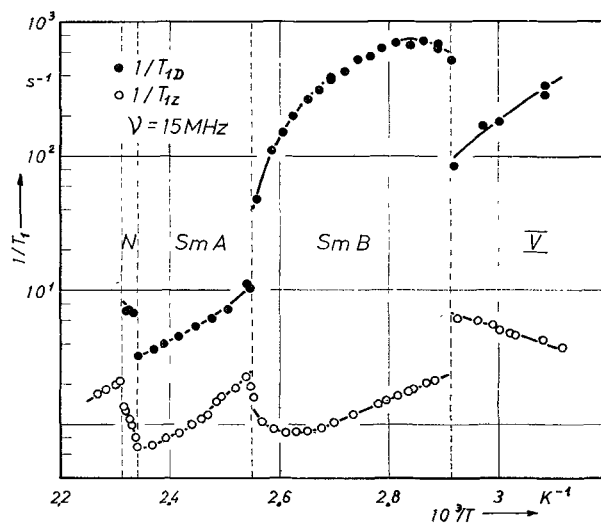


Fig. 1. — Proton Zeeman and dipolar relaxation rates of EBAC vs. reciprocal temperature. Transition temperatures are indicated by broken lines.

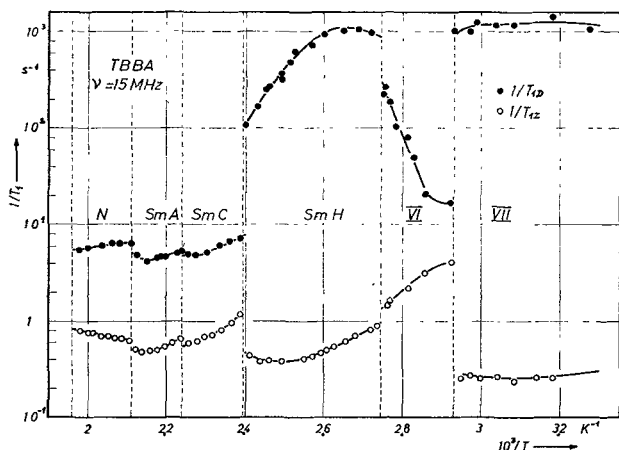


FIG. 2. — Same as figure 1 for TBBA.

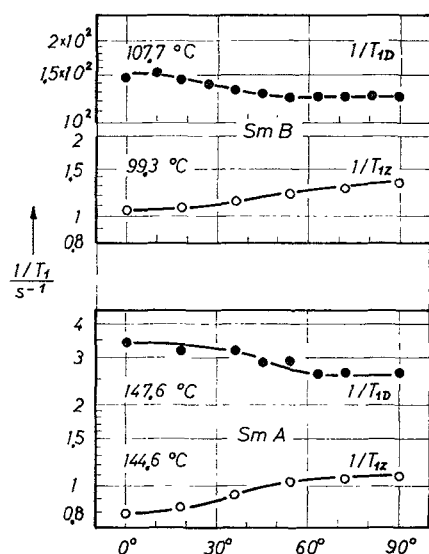


FIG. 3. — Angular dependence of Zeeman and dipolar relaxation rates in the smectic A and B phases of EBAC.

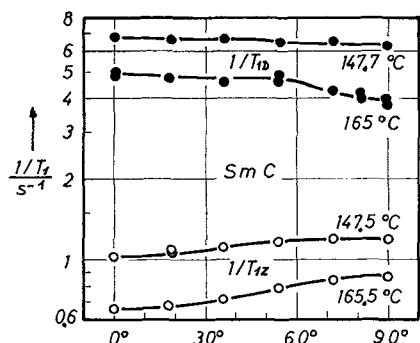


FIG. 4. — Same as figure 3 for the smectic C phase of TBBA.

the slopes of  $1/T_{1Z}$  and  $1/T_{1D}$  seem to be the same, whereas in TBBA they are opposite. In corresponding smectic phases, both substances show a similar behaviour. Each phase transition is characterized by a discontinuity in the relaxation rates. This discontinuity

is small at the N to A and at the A to C transition and much larger at the C to H and H to VI transitions in TBBA and, for  $1/T_{1D}$ , at the A to B transition in EBAC.

In EBAC both relaxation rates show similar angular dependence in the smectic A and the smectic B phase (Fig. 3). In TBBA the angular dependence in smectic A is similar to that in EBAC. In smectic C, however, the angular dependence is smaller at low temperature. This is even more pronounced for  $1/T_{1D}$  (Fig. 4).

**3.2 DIFFUSION.** — Figures 5 and 6 show the temperature dependence of the self diffusion coefficients. In the smectic phases both  $D_{||}$  and  $D_{\perp}$  obey an Arrhe-

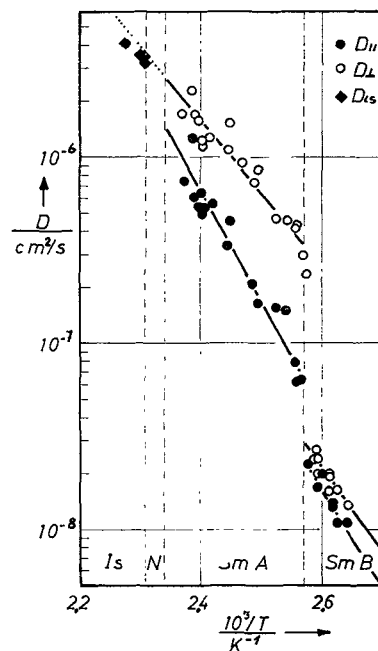


FIG. 5. — Self diffusion coefficients of EBAC vs. reciprocal temperature. Transition temperatures are indicated by broken lines.

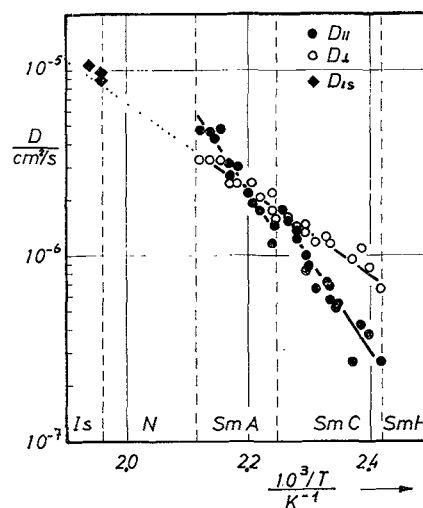


FIG. 6. — Same as figure 5 for TBBA.

nus type activation law. The activation energies  $E_{\parallel}$  and  $E_{\perp}$  and the pre-exponential factors  $D_{\parallel 0}$  and  $D_{\perp 0}$  have been determined by least squares fits and are given in table I. These values were used for the lines

TABLE I

Activation energies in kcal/mole and pre-exponential factors in  $\text{cm}^2/\text{s}$  of the diffusion coefficients.  
The errors are the probable errors of the least squares fits

Sub- stance	Phase	$E_{\parallel}$	$E_{\perp}$	$D_{\parallel 0}$	$D_{\perp 0}$
EBAC	SmA	$25.9 \pm 1.1$	$17.8 \pm 0.9$	$2.34 \times 10^7$	$3.26 \times 10^3$
EBAC	SmB	$21.6 \pm 2.8$	$20.6 \pm 2.4$	$3.08 \times 10^4$	$1.1 \times 10^4$
TBBA	SmA	$22.8 \pm 1.1$	$10.1 \pm 0.3$	$1.93 \times 10^5$	0.167
TBBA	SmC	$22.7 \pm 1.2$	$10.1 \pm 0.3$	$2.36 \times 10^5$	0.167

drawn in the figures. Extrapolation of these lines into the isotropic regime shows that the measured isotropic diffusion coefficients  $D_{is}$  lie approximately on the line of  $D_{\perp}$ . This behaviour was already shown in other systems [1, 2, 6]. In the smectic A and C phases we find  $E_{\parallel} > E_{\perp}$ . This effect is less pronounced in the smectic B phase of EBAC, but here the measuring accuracy is worse and the temperature range measured is much smaller than in the other phases. At the smectic A to C transition in TBBA we have a small discontinuity of  $D_{\parallel}$  and no observable discontinuity of  $D_{\perp}$ . Our results are in quite good agreement with neutron scattering data in TBBA [5], they are in fair agreement with NMR data obtained by a multipulse sequence in the smectic C phase [3]. In the smectic A phase, however, we are at variance with the multipulse technique data [3]. At the smectic A to B transition in EBAC we find a discontinuity of one order of magnitude of both  $D_{\parallel}$  and  $D_{\perp}$ .

**4. Discussion.** — **4.1 NEMATIC PHASE.** — As already mentioned, the Zeeman and dipolar relaxation in TBBA show opposite slopes as a function of temperature. According to [4] the slow decrease in  $1/T_{1Z}$  with increasing  $1/T$  is most probably due to a mechanism in which fluctuation of the nematic order is predominant. This is probably also true for both  $T_{1Z}$  and  $T_{1D}$  in EBAC. The behaviour of  $T_{1D}$  in TBBA on the other hand is not incompatible with relaxation by diffusion. However more complicated mechanisms involving cybotactic smectic clusters in the nematic phase could also be present. These could provide slow motions effective in relaxing the dipolar energy.

**4.2 SMECTIC A AND C PHASES.** — Since we find that  $D_{is}$  corresponds to  $D_{\perp}$  in these phases in both EBAC and TBBA we assume that the diffusion inside the smectic A and C planes is more liquid like than that out of the planes. Therefore we obtain for the ratio of the diffusion coefficients :

$$\frac{D_{\parallel}}{D_{\perp}} = 2 \frac{\langle r_{\parallel}^2 \rangle \tau_{\perp 0}}{\langle r_{\perp}^2 \rangle \tau_{\parallel 0}} \exp [-(E_{\parallel} - E_{\perp})/RT]. \quad (1)$$

Here  $\langle r_{\parallel}^2 \rangle$  is the mean square displacement out of the plane and  $\langle r_{\perp}^2 \rangle$  is the mean square displacement in the plane.  $\tau_{\parallel 0}$  and  $\tau_{\perp 0}$  are the pre-exponential factors of the jump times. If we take  $E_{\parallel}$  and  $E_{\perp}$  from table I we find that in our temperature range

$$3 \times 10^{-7} \leq \exp [-(E_{\parallel} - E_{\perp})/RT] \leq 7 \times 10^{-5}. \quad (2)$$

Since  $D_{\parallel}$  and  $D_{\perp}$  have the same order of magnitude we get

$$10^4 \leq 2 \frac{\langle r_{\parallel}^2 \rangle \tau_{\perp 0}}{\langle r_{\perp}^2 \rangle \tau_{\parallel 0}} \leq 3 \times 10^6. \quad (3)$$

This condition can be fulfilled if  $\langle r_{\perp}^2 \rangle \ll \langle r_{\parallel}^2 \rangle$  and/or  $\tau_{\parallel 0} \ll \tau_{\perp 0}$ . We think that this supports our assumption of liquid like diffusion in the plane : If  $\langle r_{\parallel}^2 \rangle \approx l^2$  ( $l$  = length of the molecules) and  $\langle r_{\perp}^2 \rangle \approx d^2$  ( $d$  = diameter of the molecules) we are, in the planes, in the limiting case of the random flight theory [9, 10], where the diffusion jumps are very small compared with the molecular dimensions and have very short jump times. They are, however, correlated and the correlation time can be much longer than the jump time [10, 11]. In fact it can be as large as the jump time  $\tau_{\parallel}$  out of the plane. If we assume  $l \approx 30 \text{ \AA}$  and  $D_{\parallel}$  between  $10^{-5}$  and  $10^{-7} \text{ cm}^2/\text{s}$  we obtain  $\tau_{\parallel}$  between  $4 \times 10^{-9}$  and  $4 \times 10^{-7} \text{ s}$ .

At 15 MHz, where our relaxation times were measured, we have  $\omega^{-1} \approx 10^{-8} \text{ s}$ . Therefore the diffusion must contribute to the relaxation. We interpret the minimum in the  $1/T_{1Z}$  and  $1/T_{1D}$  curves in the smectic A phase of TBBA as originating from a competition between order fluctuation and self diffusion mechanism, the last being predominant at low temperature. Further evidence for this is given by : 1) the discontinuities of the relaxation rates and  $D_{\parallel}$ , at the A to C phase transition in TBBA, which are about equal and go in the same direction and 2) the activation energies of  $1/T_{1D}$  at the low temperature side of the smectic C phase of TBBA and smectic A phase of EBAC which lie within the activation energies of  $D_{\parallel}$  and  $D_{\perp}$  in the same phases.

The angular dependence of  $1/T_{1Z}$  is compatible with a mechanism of the type *diffusion induced order fluctuation relaxation* [4], that of  $1/T_{1D}$ , however, does not show the typical behaviour associated with that mechanism. In the smectic C phase the angular variations of  $1/T_{1Z}$  and  $1/T_{1D}$  are smoothed by decreasing the temperature. This, most probably, reflects the ability of the molecules to partially follow the field direction by turning along a cone generator while keeping the tilt angle constant. This capability of the molecular director to follow the field will evidently increase with increase of the tilt angle (decrease of the temperature). Such a behaviour was also considered in reference [8] to explain the angular dependence of the free induction decay in smectic C phases.

**4.3 SMECTIC B AND H PHASES.** — In contrast to the

smectic A and C phases we think that the diffusion process inside the smectic B planes of EBAC is a jump process with jump lengths of the order of the molecular diameter. Therefore, in this case the pseudolattice model of R. Blinc *et al.* [3] can be applied which gives :

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{l}{d} \exp[-(E_{\parallel} - E_{\perp})/RT] . \quad (4)$$

In fact, now the difference of activation energies is small and  $\exp[-(E_{\parallel} - E_{\perp})/RT]$  is no longer so small as before but rather close to unity. With  $l/d \approx 5$  we arrive at  $D_{\parallel} \approx D_{\perp}$ , which is in fact what we observe (Fig. 5). The relaxation mechanism of  $1/T_{1D}$  seems to be diffusion because we have similar activation energies for  $1/T_{1D}$  and the diffusion coefficients in the temperature region where these have been measured. This assumption is also supported by two other facts. First the discontinuity of  $1/T_{1D}$  and of the diffusion coefficients at the A to B phase transition of EBAC are about equal and go in the same direction, second if we extrapolate the activation law of  $D_{\parallel}$  to the temperature where the maximum of  $1/T_{1D}$  occurs and assume a jump length of about 30 Å we get  $\tau_{\parallel} \approx 3 \times 10^{-5}$  s

which corresponds to the  $T_2^*$  observed in the free induction decay. Since the behaviour of  $1/T_{1D}$  in the smectic H phase of TBBA is very similar we assume that it is also due to the diffusion process, though we were not able to measure the diffusion coefficients in that phase. For both EBAC and TBBA the Zeeman behaviour is probably a mixture of diffusion and chain rotation at the low temperature side.

**4.4 LOW TEMPERATURE PHASES.** — In phase VI of TBBA  $1/T_{1D}$  shows a very large activation energy (45.7 kcal/mole). This can be due either to a rotation of the benzene rings [12] or to a diffusion in a solid like structure.  $1/T_{1Z}$  may again be due to chain rotation. The relaxation mechanisms in phases VII of TBBA and V of EBAC are not clear, we can state, however, that there is a strong contribution of slow motions to  $1/T_{1D}$  in both cases, whereas TBBA must have rather fast motions contributing to  $1/T_{1Z}$  (e. g.  $\text{CH}_3$ -rotation).

**Acknowledgments.** — The authors would like to thank Mr. J. Cametti and Mr. R. Weiss for their valuable help with the measurements and Dr. G. A. Helcké for revision of the manuscript.

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