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PROTON T_1 NMR INVESTIGATION OF ORDER FLUCTUATIONS, SELF-DIFFUSION AND ROTATIONAL MOTIONS IN ISOTROPIC MBBA AND EBBA

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Résumé. — Nous avons mesuré la dispersion du temps de relaxation des protons, $T_1(\nu)$, dans la phase isotrope de MBBA et EBBA dans un intervalle de fréquence de Larmor plus étendu qu'auparavant. Les résultats sont discutés en fonction des fluctuations de l'ordre, de l'auto-diffusion et des mouvements rotatoires. Les temps de corrélation évalués ne sont pas en plein accord avec les résultats obtenus par des méthodes spectroscopiques différentes.

Abstract. — We have made measurements of the proton spin relaxation dispersion, $T_1(\nu)$, in the isotropic phase of MBBA and EBBA, over a more extended Larmor frequency range than previous workers. The data are discussed in terms of order fluctuations, self-diffusion and rotational motions by means of computer model fittings. Correlation times obtained in this way do not show full agreement with the results of other spectroscopic techniques and previous NMR studies.

1. Introduction. — NMR relaxation studies of the molecular dynamics of isotropic MBBA have led to rather different interpretations up to now. The complex Larmor frequency dependence and the non-Arrhenius temperature dependence of the proton spin relaxation time T_1 , observed previously by other research groups, were successively attributed to self-diffusion [1], non-local (BPP-type) order fluctuations [2], local (Cabane-type) order fluctuations [3], a superposition of local and non-local order fluctuations combined with a very unusual diffusion mechanism [4] or recently to local and non-local order fluctuations superimposed by a frequency independent diffusional contribution [5].

Similar to our wide frequency range investigation of *nematic* MBBA and PAA [6] we have made measurements of the proton T_1 relaxation dispersion in the isotropic phase of MBBA and EBBA in order to find out whether additional experimental data would allow more clear-cut conclusions. To understand the dilemma it should be realized that the controversial models were developed using measurements over a rather narrow frequency range in the conventional MHz regime, where the experimental effects seem to be too small for a critical analysis. Field cycling techniques allows one to extend this range considerably. By comparing the relaxation dispersion of the homologous liquid crystals MBBA and EBBA we hoped to get additional criteria to separate the possible contributions to the total relaxation rate, since the different clearing points of the closely related nematogens should result in well defined

changes of the various mechanisms. Previous interpretations of the rather limited experimental data for EBBA were based on self-diffusion and rotational motions [7].

2. Experimental techniques and results. — Proton relaxation times, T_1 , for isotropic MBBA and EBBA were measured at temperatures from 0.5 °C to 30 °C above the clearing points (EBBA : 77.9 °C, MBBA : 46.5 °C) over a Larmor frequency range from about 1 kHz to 270 MHz. The measurements below 100 MHz were made with a home-built pulsed spectrometer described elsewhere [8], using field cycling techniques in the low-frequency regime and standard NMR pulse programs in the high-frequency regime. At 270 MHz, T_1 's of the individual lines of the spectra were obtained by means of a Bruker Fourier transform spectrometer using the progressive saturation method.

It is now well-confirmed that *nonselective* proton spin relaxation decays in the isotropic phase of liquid crystals are multiexponential [9], and that *selective* studies of the phenyl, alkyl and methyl protons yield different relaxation rates [9]. However, the degree of nonexponentiality and the related differences between the individual T_{1i} 's are not easily seen and, hence, up to the present we were unable to separate the contributions in the *low-frequency range* of our spectrometer, since below 450 kHz the signal-to-noise ratio became too low for such analysis. So we decided to evaluate the

decay curves for *all* Larmor-frequencies by means of a single T_1 by considering only the initial slope of the nonselective relaxation plots or the weighted mean value of the selective Fourier transform measurements.

The T_1 data obtained in this way are presented as a function of proton Larmor frequency $\nu \equiv \omega/2\pi$ at 4 temperatures above the clearing point θ_c in figure 1 (MBBA) and figure 2 (EBBA). Each data point of the diagrams is the average of several T_1 runs. Estimated from the root mean square deviation the accuracy of the results shown is better than $\pm 7\%$ above and about $\pm 10\%$ below 450 kHz.

The findings for MBBA and EBBA are qualitatively very similar: Due to the different clearing points of the nematogens the relaxation times are longer for EBBA than for MBBA, and the T_1 dispersion is somewhat shifted to higher ν values. Obviously, at least two relaxation regimes can be distinguished in both cases. Whereas at low frequencies the relaxation times are independent of the Larmor frequency but strongly dependent on the temperature, one almost observes the opposite behaviour at high frequencies. It should be noted that in the MHz range our new results essentially agree with the T_1 values reported previously in the literature [1-5, 7].

3. Discussion. — 3.1 RELAXATION MODEL. — The basic ideas of proton spin relaxation in the isotropic phase of nematogen liquid crystals have been excellently reviewed recently [4, 5, 10, 11, 12]. However, some comments on the theoretical background are necessary in order that the model used for curve fits to the new experimental data becomes clear. At present, 4 types of molecular reorientations have been suggested as possible contributors to the relaxation rate, namely the Cabane order fluctuation mechanism (OF_1), the BPP order fluctuation mechanism (OF_2), molecular self-diffusion (SD), and rotational motions (R). In view of the numerous parameters involved, the available experimental T_1 data do not allow an unambiguous separation of these 4 processes without additional information, in particular because of the identical relaxation dispersion predicted by the OF_2 - and R-model, respectively. Therefore, we decided to try curve fits in terms of only 3 mechanisms, namely OF_1 , SD, and OF_2 or R. Treating for simplicity all protons as equivalent (a more detailed discussion will be given elsewhere), and assuming the reorientations to be independent, standard relaxation theory of proton spins undergoing different types of isotropic motions gives the well-known relations [13]

$$\frac{1}{T_1} = \sum_j^3 \frac{1}{T_{1,j}} \quad (1a)$$

$$\frac{1}{T_{1,j}} = \frac{9}{8} \gamma^4 \hbar^2 [J_j^{(1)}(\omega) + J_j^{(2)}(2\omega)] \quad (1b)$$

$$J_j^{(2)}(\omega) = 4 J_j^{(1)}(\omega), \quad (1c)$$

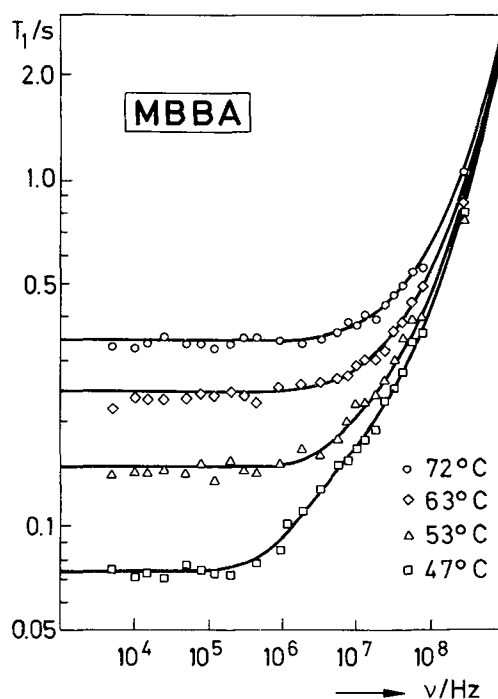


FIG. 1. — Proton spin relaxation dispersion, $T_1(\nu)$, for isotropic MBBA at 4 temperatures above the clearing point. Data points: Experimental results. Curves: Computer fit of the OF_1 -SD- OF_2 model, eqs. (1)-(7), with parameters listed in table I.

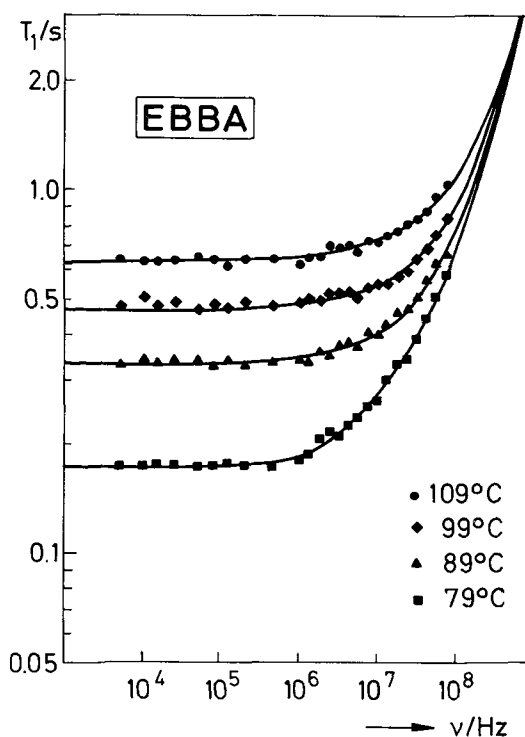


FIG. 2. — Proton spin relaxation dispersion, $T_1(\nu)$, for isotropic EBBA at 4 temperatures above the clearing point. Data points: Experimental results. Curves: Computer fit of the OF_1 -SD- OF_2 model, eqs. (1)-(7), with parameters listed in table I.

where in the present case j refers to either OF_1 , SD or OF_2/R (γ : proton magnetogyric ratio ; $J_j^{(0)}(\omega)$: Fourier intensities of proton-proton interaction). Numerous approaches to these intensity spectra $J_j^{(0)}(\omega)$ have been proposed in the literature. We made use of the following model based on the assumption that the 3 motions are independent and that the interaction between proton spins is purely dipolar [4-6, 11-13]

$$J_{OF_1}^{(1)} = \frac{A_1}{R^6} \frac{\tau_1^{1/2}}{[1 + (1 + \omega^2 \tau_1^2)^{1/2}]^{1/2}} \quad (2)$$

$$J_{SD}^{(1)} = \frac{16\pi}{15} \frac{N}{d^3} \times \int_0^\infty \frac{[B_{3/2}(\rho d)]^2}{\rho} \frac{3 \tau_{SD}/(\rho d)^2}{1 + [3 \omega \tau_{SD}/(\rho d)^2]^2} d\rho \quad (3)$$

$$J_{OF_2,R}^{(1)} = \frac{A_2}{R^6} \frac{\tau_2}{1 + \omega^2 \tau_2^2} \quad (4)$$

The notation is as follows : R : average proton-proton distance ; τ_1 , τ_2 , and τ_{SD} : correlation times of the considered reorientations ; N : proton number density ; d : distance of closest proton approach for diffusion ; $B_{3/2}$: Bessel function of order 3/2 ; A_1 , A_2 : constants depending on the molecular geometry and the liquid crystalline structure (i.e. on the order parameter, viscosity, elastic moduli etc.).

3.2 CURVE FITTING. — To test the model described above we fitted eqs. (1)-(4) to the experimental T_1 's shown in figures 1 and 2 by treating the 6 quantities A_1/R^6 , A_2/R^6 , d , τ_1 , τ_{SD} , and τ_2 as adjustable parameters, whereas N was taken from the molecular geometry. (MBBA : $0.05 \text{ \AA}^{-3}$; EBBA : $0.048 \text{ \AA}^{-3}$.) The fits were achieved by a special computer technique [14] which minimizes the sum of squares of deviations between the experimental and theoretical

cal T_1 values and thereby finds the best model parameters. Since the independent curve fitting at the individual temperatures did not give satisfactory results we extended the computer procedure to the simultaneous analysis of *both* the frequency *and* the temperature dependence of the data points by utilizing theoretical predictions on the changes of A_1/R^6 , ..., τ_2 as a function of the absolute temperature θ . This considerably improved the quality of the curve fits. Following standard theories on phase transitions and rate processes [15], we incorporated the following relations into eqs. (2)-(4) :

$$A_1/R^6 = \frac{A_0}{(\frac{9}{8} \gamma^4 \hbar^2)} \theta \exp\left(\frac{1}{2} E_v/k\theta\right) \quad (5a)$$

$$\tau_1 = \tau_{10} \cdot \frac{\exp(E_v/k\theta)}{\theta - \theta^*} \quad (5b)$$

$$\tau_{SD} = \tau_{SD0} \cdot \exp(E_{SD}/k\theta) \quad (6a)$$

$$d = d_0 \quad (6b)$$

$$A_2/R^6 = \frac{B_0}{(\frac{9}{8} \gamma^4 \hbar^2)} \quad (7a)$$

$$\tau_2 = \begin{cases} \frac{\tau_{20} \exp(E_v/k\theta)}{\theta - \theta^*}, & (\text{OF}_2 \text{ model}) \\ \tau_{20} \exp(E_R/k\theta), & (\text{R model}). \end{cases} \quad (7b) \quad (7c)$$

The temperature independent constants A_0 and B_0 (amplitude factors ; the factor $\frac{9}{8} \gamma^4 \hbar^2$ is included for convenience), τ_{10} , τ_{SD0} and τ_{20} (preexponential factors), E_v ($\hat{=}$ $E_{OF_1} = E_{OF_2}$), E_{SD} and E_R (activation energies), d_0 (distance of closest approach), and θ^* (effective phase transition temperature), all characteristics of the molecular reorientations, were treated as adjustable model parameters. Table I summarizes the final numerical results, and the full lines in figures 1 and 2 illustrate the quality of the fit for the case that τ_2 is interpreted in terms of OF_2 (eq. (7b)). However, replacing eq. (7b) by eq. (7c) has only little effect on the minimum least squares deviation, more precise measurements in the immediate vicinity of $\theta_c \approx \theta^*$ are necessary for a critical analysis. In addition to the full diagram, figures 3 and 4 show T_1 for MBBA at 47 °C and 53 °C together with the individual contributions T_{1,OF_1} , $T_{1,SD}$, and T_{1,OF_2} . For comparison, Dong's results [4] based on the evaluation of measurements only in the MHz regime is also shown in the last figure.

3.3 CONCLUSIONS. — A critical estimation of the model fittings demonstrates that T_1 relaxation dispersion over a wide frequency range in isotropic MBBA and EBBA can only be described by a superposition of at least two frequency dependent contributions, one necessarily being diffusional ($T_{1,SD}$). The combination of the OF_1 and SD contribution with a third mechanism, either OF_2 or R, slightly improves the quality of the fit, in particular the low-temperature data. However, the additional term is so small that despite of the differing temperature

TABLE I

Parameters of the OF_1 -SD- OF_2 relaxation model, eqs. (1)-(7), evaluated from the T_1 dispersion in isotropic MBBA and EBBA, figures 1 and 2, by computer optimization

Type of motion	Parameter	MBBA	EBBA
SD	τ_{SD0}/s	3.2×10^{-15}	8.0×10^{-15}
	$E_{SD}/\text{kJ/mol}$	33.5	33.1
	$d/\text{\AA}$	3.47	3.54
	$\tau_{10}/s \cdot K$	2.5×10^{-11}	1.1×10^{-11}
OF_1	$E_v/\text{kJ/mol}$	23.4	27.0
	θ^*/K	318.16	350.56
	$A_0/s^{-3/2}$	0.165	0.088 9
	$\tau_{20}/s \cdot K$	2.9×10^{-11}	(T_{1,OF_2}^{-1} too small)
OF_2	B_0/s	9.2×10^6	

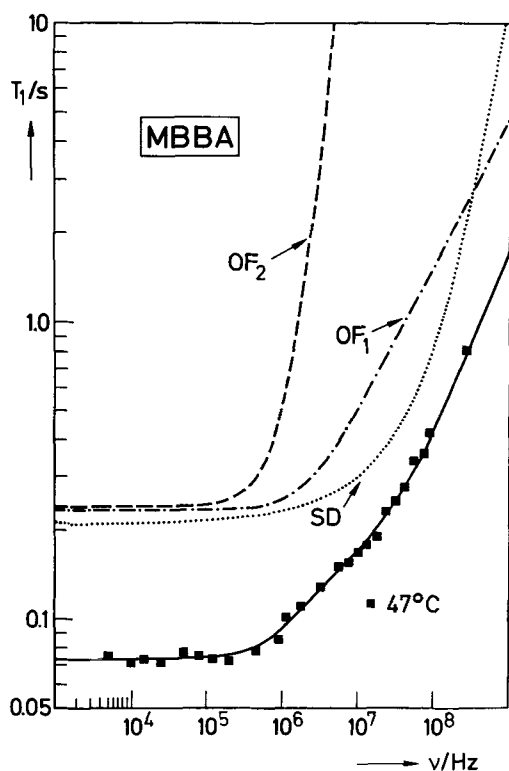


FIG. 3. — Proton spin relaxation dispersion, $T_1(v)$, for isotropic MBBA at 47 °C from figure 1 and individual contributions T_{1,OF_1} , $T_{1,SD}$ and T_{1,OF_2} .

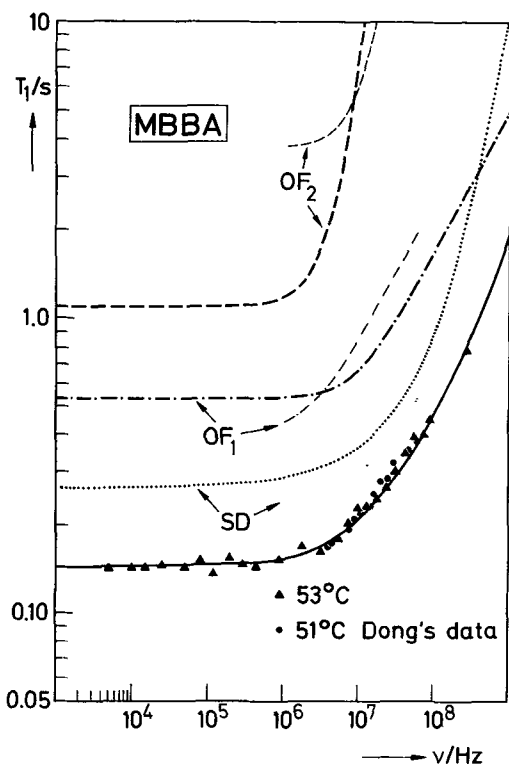


FIG. 4. — Proton spin relaxation dispersion, $T_1(v)$, for isotropic MBBA at 53 °C from figure 1 and individual contributions T_{1,OF_1} , $T_{1,SD}$ and T_{1,OF_2} in comparison with Dong's analysis at 51 °C [4].

characteristics of T_{1,OF_2} and $T_{1,R}$ (critical or Arrhenius-like) no preference can be given to either refinement from the NMR results alone. Our analysis essentially confirms and refines Dong's treatment [4] of isotropic MBBA by means of the Ghosh formalism [2], but contrasts with Ghosh's conclusions [5] that the $T_{1,SD}$ contribution is independent of the Larmor frequency.

A not quite satisfactory picture develops if one compares the correlation times τ_1 and τ_{SD} derived in the present NMR study (table I) with data obtained from other spectroscopic methods. On the one hand both optical studies [16] and NMR pulse gradient investigations [17] give diffusion coefficients higher (or correlation times shorter) by a factor of about 3.1 ... 4.7 than expected from the relation

$$D = d^2/(6 \tau_{SD})$$

[e.g. MBBA, 53 °C :

$$D_{T_1, NMR} = 2.7 \times 10^{-7} \text{ cm}^2/\text{s};$$

$$D_{opt} = 8.5 \dots 8.6 \times 10^{-7} \text{ cm}^2/\text{s};$$

$$D_{pulseNMR} = 9.8 \dots 12.7 \times 10^{-7} \text{ cm}^2/\text{s}].$$

The related activation energies essentially show no discrepancy within the experimental error limits. On the other hand, optical τ_1 data [18] are appreciably longer than our T_1 results, namely by a factor of 3.6 ... 10 [e.g. MBBA, 53 °C $\simeq \theta^* + 8.5$ °C : $\tau_{1,T_1, NMR} = 1.7 \times 10^{-8}$ s ; $\tau_{1,opt} = 4.3 \dots 18 \times 10^{-8}$ s] ; the origin of these deviations is not clear. The third time constant, τ_2 , does not allow a critical check because of the lack of quantitative measurements. However, following Ghosh [5] its value [e.g. MBBA 53 °C : $\tau_2 = 2.0 \times 10^{-8}$ s] is not unreasonable if interpreted in terms of the OF_2 -model and compares rather well with Dong's analysis [4]. Rotational motions in the isotropic phase are expected to be much faster [19].

A comparison of the MBBA and EBBA model parameters reveals that the relative data agree much better with conclusions of other works than the absolute ones. Both the ratio of the diffusional correlation times at constant temperature [e.g. 80 °C : $\tau_{SD, MBBA}/\tau_{SD, EBBA} = 0.49$] and the ratio of the order fluctuation correlation times at constant deviation $\theta - \theta^*$ [e.g. 1.6 °C : $\tau_{1, MBBA}/\tau_{1, EBBA} = 1.59$] are very similar to the findings of NMR pulse gradient [17] and optical investigations [18]. In our opinion this is a decisive argument for the essential validity of the suggested model despite its obvious shortcomings. Most probably these are due to the neglect of the nonexponentiality of the relaxation process.

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