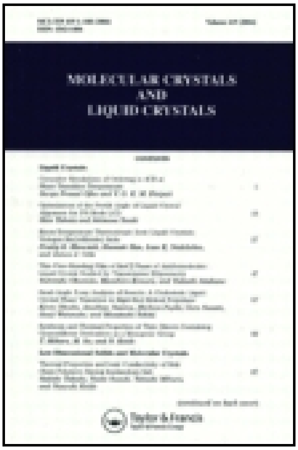

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: F. Rondelez & A. Mircea-roussel (1974): Dielectric Relaxation in the Radio Frequency Range for the Nematic Phase of M.B.B.A., Molecular Crystals and Liquid Crystals, 28:1-2, 173-178

To link to this article: http://dx.doi.org/10.1080/15421407408083162

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 173-178

Printed in Dordrecht, Holland

Dielectric Relaxation in the Radio Frequency Range for the Nematic Phase of M.B.B.A.[†]

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(*Received September 4, 1973*)

The dipolar relaxation for the component $\epsilon_{/\!/}$ of dielectric tensor has been studied in nematic phase of p-methoxy benzylidene p-n butyl-aniline oriented by a magnetic field.

A low frequency relaxation process corresponding to the rotational diffusion of the molecules around one of their short axes is observed. Our results are consistent with the existence of a single relaxation frequency, in the range 100 kHz – 10 MHz. The temperature dependence of this frequency can be described by an activation energy W = 0.65 ± 0.05 eV. These results contradict previous data, which have to be corrected (F. Rondelez *et al*, MOL. CRYST. and LIQ. CRYST. 15, 183 (1971)).

In a previous paper, Rondelez, Diguet and Durand[1] have studied the dielectric relaxation in the room temperature nematic material p-methoxy benzilidene p-n butyl aniline (M.B.B.A. for short). In the frequency range actually investigated -100 kHz to 10 MHz- a relaxation process has been observed for the component $\epsilon_{/\!/}$ of the dielectric tensor and none for $\epsilon_{\perp}$; $\epsilon_{/\!/}$ and $\epsilon_{\perp}$ are the static dielectric constants parallel and perpendicular to the direction of the nematic alignment.

These results are well accounted for by the assumption of Maier and Meier[2] which states that, due to the nematic ordering, rotation around a short molecular axis takes much longer time than around the long molecular axis. As the M.B.B.A. molecules have a non-zero component of permanent electric dipole

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[†] work supported partly by Direction des Recherches et Moyens d'Essais under contract no. 72 34 208 00 480 75 01.

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along their long axis[3], a relaxation of orientational polarization in the radiofrequency range can be observed for $\epsilon_{/\!/}$, while the dipolar relaxation for $\epsilon_{\perp}$ occurs at higher frequencies in a range similar to the case of isotropic liquids.

The existence of this low-frequency relaxation has been observed in various compounds[1, 2, 4, 5]. However, the data for dielectric relaxation in M.B.B.A., as given in ref. 1, have been questioned recently by Price[6] who has observed that the variations of the real and imaginary parts of the dielectric constant $\epsilon_{/\!/} = \epsilon'_{/\!/} + i\epsilon''_{/\!/}$ do not fulfil Kramer-Krönig relations. This was due to errors in correcting for lumped impedances at high frequency. So, we decided to resume this experiment using a new experimental set-up together with a different method to analyse the experimental data.

All measurements have been done on M.B.B.A. with a clearing point of 45°C. But the temperature for measurements in the nematic phase of M.B.B.A. was only varied between 22°C and 42°C because our apparatus does not permit the study of the high relaxation frequencies involved close to the clearing point.

The cell arrangement has been described in full details elsewhere[7]. Compared with our previous experiments, we use the same parallel plate geometry but the whole system is now teflon-insulated to minimize the losses at high frequency. The electrodes consist of two massive copper blocks coated with evaporated gold layers to lower the resistance in series with the liquid crystal layer below 1 Ω. The sample is inserted in an electrically-heated furnace regulated within 0.1°C and with an over-all temperature gradient of about 0.5°C. The whole set-up can be rotated between the poles of a 44 mm gap electromagnet achieving fields up to 12 kG. According to the geometry, the molecules are aligned with their long axis either parallel or perpendicular to the applied electric field, and the components $\epsilon'_{/\!/}$ or $\epsilon'_{\perp}$ are respectively measured together with the associated dielectric losses $\epsilon''_{/\!/}$ and $\epsilon''_{\perp}$.

A coaxial line connects the cell to a Wayne Kerr B 602 capacitance bridge which is fitted with a source and a detector of the same make. The input plugs have been modified to be adapted to a coaxial line. The practical frequency range is between 100 kHz and 8 MHz and this allows to measure relaxation frequency, f_R, not higher than 5 MHz.

The values for ϵ' and ϵ'' are not obtained straight from the experimental results. Besides corrections for lumped impedances due to the finite length of the coaxial line compared to the wavelength of measurement, corrections for the ionic conductivity of the sample have to be taken into account. This is most simply acieved by measuring both $\epsilon_{/\!/}$ and $\epsilon_{\perp}$ at each frequency. As we know that $\epsilon_{\perp}$ exhibits no relaxation process over the whole frequency range in the present study, $\epsilon'_{\perp}$ must be found to be constant and the dielectric losses $\epsilon''_{\perp}$ must be zero. Actually, measuring $\epsilon'_{\perp}$ and $\epsilon''_{\perp}$, we observe that while $\epsilon'_{\perp}$ is practically constant with frequency as expected, $\epsilon''_{\perp}$ is non-zero. At low frequency, this is due to the non-zero ionic conductivity; however, this effect decreases as f^{-1} and at frequencies above 1 MHz it is completely negligible compared to a systematic deviation caused by the equipment itself and by the connecting leads. These non-zero values for $\epsilon_\perp''$ are used to correct the $\epsilon_{\parallel}''$ values. This method gives good results, quite reproducible from one sample to another from the same batch.

The accuracy for the determination of f_R is estimated to be ± 100 kHz. The relative variations of $\epsilon_{\parallel}$ between 1 and 8 MHz are given to ± 2%. The absolute values are given to ± 6% taking into account the errors on evaluation of the surface and thickness of the cell, and the bridge inaccuracy.

RESULTS

Figure 1 displays our results for the real and imaginary parts of the dielectric constant $\epsilon_{\parallel}$ versus frequency. For M.B.B.A., at T = 22.75°C a relaxation process clearly occurs at 1.1 MHz for the longitudinal component of the static dielectric tensor. The $\epsilon_{\parallel}'$ curve drops from a low-frequency value ϵ_0 to a high frequency value ϵ_1. The variation $\Delta\epsilon = \epsilon_0 - \epsilon_1$ amounts to 0.4. The $\epsilon_{\parallel}''$ curve shows a maximun $\epsilon''_{max} = 0.2$ at the relaxation frequency f_R. This was expected from Debye's theory[8] which predicts $\epsilon''_{\parallel max} = \frac{\Delta\epsilon}{2}$. Plotting $\epsilon_{\parallel}''$ versus $\epsilon_{\parallel}'$ for various

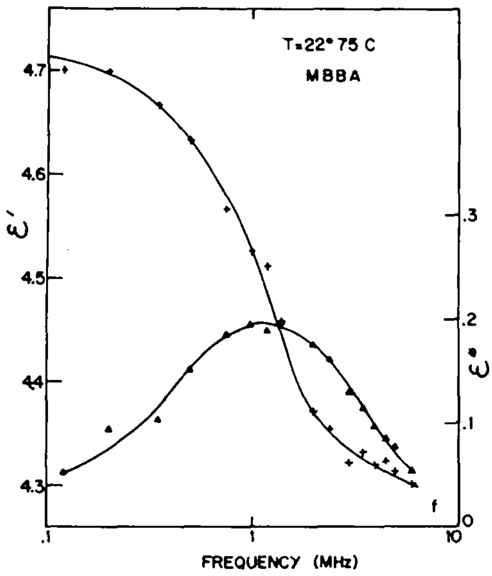

FIGURE 1 Frequency dependence of the real (ϵ') and imaginary part (ϵ'') of the dielectric constant parallel to the long molecular axis ($\epsilon_{\parallel}$) for M.B.B.A. The temperature is 22.75°C. The sample thickness is 100 μm.

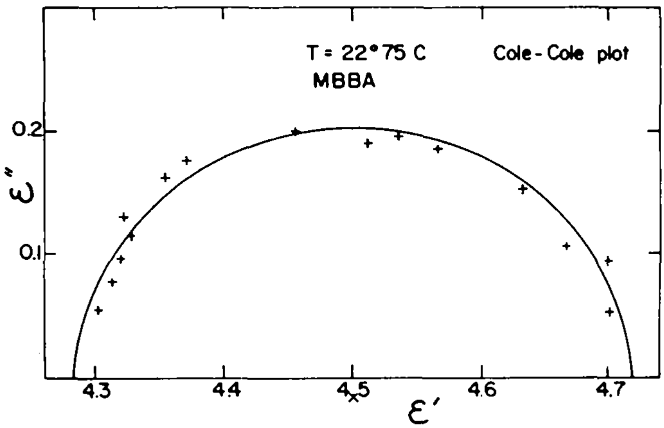

FIGURE 2 Cole-Cole plot for the real and imaginary part of the dielectric constant parallel to the long molecular axis ($\epsilon_{\parallel}$) for M.B.B.A. The experimental conditions are the same as for Figure 1.

frequencies, good Cole-Cole arcs are obtained. We get semi-circles which means the relaxation process can be characterized by a single relaxation frequency f_R. This Cole-Cole plot allows for an easy determination of ϵ_1 when this parameter cannot be obtained within the range of the bridge. Knowing the values of ϵ_0, ϵ_1 and f_R, the relaxation process is entirely described. The temperature dependence of f_R between 22°C and 42°C is shown on Figure 3. From this Arrhenius plot, it is clear the relaxation process can be described by an activation energy W, as defined by $f_R \,\alpha\, \exp\frac{-W}{kT}$. W is found to be 0.65 ± 0.05 eV.

This value is significantly different that of 1.1 eV obtained from our previous data[1]. This new value is in the same range as those reported by Schadt[4] for a mixture of Schiff Bases and by de Jeu and Lathouwers[5] for various nematic phenyl benzoates. Higher values for W have been reported[7] for the higher homologs of the di-n alkoxy azoxy benzenes which present a smectic-nematic polymorphism. W describes the height of the potentiel hill to be overcome by a molecule during a switch from an orientation parallel to antiparallel along the nematic optical axis.

DISCUSSION

Taking into account the ellipsoïdal shape of the molecules, according to Perrin's calculations[10], and the existence of the nematic ordering by inserting the friction coefficient associated with the rotation of the director, we can write the

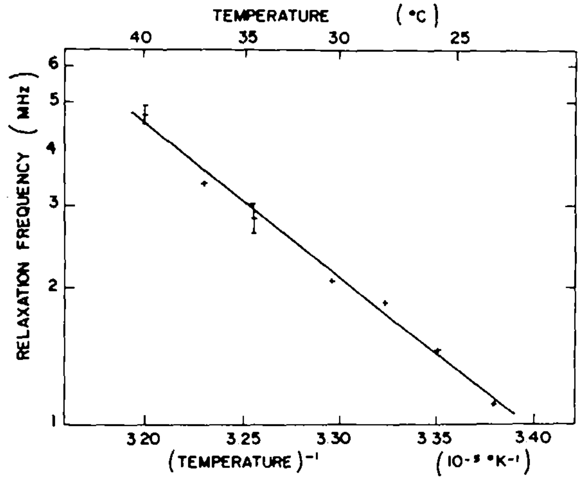

FIGURE 3 Semilog plot of the relaxation frequency for M.B.B.A. as a function of the reciprocal temperature. The solid line corresponds to an Arrhenius curve with an activation energy equal to 0.65 eV.

classical Debye's formula for the frequency of relaxation:

$$f_R = \frac{1}{2\pi} \frac{kT}{3\gamma_1} \frac{1}{V\alpha(\rho)}$$

V is the average molecular volume, $\alpha(\rho)$ is the Perrin's parameter which depends on the ratio of the principal axes of the molecules, and γ_1 is the twist viscosity coefficient. With $V = 3.9.10^{-22}$ cm^3, $\alpha(\rho) = 2.8$[10] and $\gamma_1 = 1.25 \pm 0.05$ P at 22°C[11], such a formula leads to $f_R = 1.8$ MHz, at 22°C for M.B.B.A., in rather good agreement with our measured value of 1.1 MHz. Moreover, the activation energy W associated with f_r, $W = (0.65 \pm 0.05)$ eV, is close to the one associated with γ_1 (0.5 eV to 0.8 eV according to various authors[11]).

Such an agreement does not seem to be a pure coincidence; the same remarks hold for the namatic phase of PAA: an evaluation from a Debye's formula, with $\gamma_1 = 6$ cp[12], gives $f_R = 49$ MHz at 125°C, while the measured value by Axmann[13] is 37 MHz, at the same temperature.

It is very surprising that a Debye type formula can apply, even qualitatively, for the low frequency dielectric relaxation of a nematic phase: it is well known that such a simple relation between relaxation frequency and viscosity is only valid for very dilute solutions of large dipolar rigid molecules in non polar solvents. It does not hold for pure polar liquids. For example, in PAA, the relaxation frequencies in the isotropic phase and of $\epsilon_\perp$ in the nematic phase[14], which are commonly referred to[15] as the normal Debye relaxation, are in complete disagreement with a Debye formula using the macroscopic shear viscosity. The discrepancy is of two orders of magnitude[16].

A tentative qualitative explanation might be that, due to the long range nematic ordering, the molecular rotational diffusion around one of the short molecular axis in the nematic phase does not involve rotation of individual molecules but rather cooperative rotation with displacement of several neighbouring molecules. One can then understand that the Debye model can give a first approach of the relaxation behaviour if inserting into it the macroscopic twits viscosity. Anyway, it is clear that a quantitative description of the relaxation process based on a microscopic theory is badly needed in the nematic phase.

Acknowledgments

The authors gratefully acknowledge a remark by A. H. Price which is at the origin of this new set of results. It is also a pleasure to thank G. Durand, F. Jännig and L. Léger for a critical reading of the manuscript.

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