Temperature Dependence of Anisotropic-Ultrasonic Propagation in a Nematic Liquid Crystal*

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The ultrasonic attenuation and velocity of longitudinal waves in the nematic liquid crystal *N*-*p*-methoxybenzylidine-*p*-butylaniline have been measured as a function of temperature and applied magnetic field at 3.5 MHz, between 17 and 65°C. The orientational anisotropy of the attenuation is strongly temperature dependent in the nematic phase. The velocity shows a 9% dip in the region of the transition; no anisotropy was observed within the 1% accuracy of the measurements.

Many interesting characteristics of nematic liquid crystals are associated with the anistropy of their physical properties with respect to the orientation of the long molecular axes in the mesomorphic state. Partial investigations of the anisotropy of ultrasonic absorption and velocity have been undertaken recently. In particular, Lord and Labes[1] have measured the dependence of ultrasonic attenuation on the orientation of an external magnetic field in *N*-*p*-methoxybenzylidene-*p*-butylaniline (MBBA) at room temperature, while Lieberman, Lee, and Moon[2] and Kemp and Letcher[3] have made similar measurements in *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP) in a limited temperature range.

In this paper we present the result of measurements of ultrasonic attenuation and velocity of longitudinal waves in MBBA at a frequency of 3.5 MHz, in a temperature range from 17 to 65°C (the transition temperature of the MBBA samples used was about 41°C). The measurements were carried out in zero applied magnetic field as well as with fields parallel and perpendicular to the wave-propagation vector.

The experiments were performed using a pulse-echo technique in a cylindrical, stainless-steel cell having a diameter of 1.7 cm and a variable transducer-reflector separation which was set at approximately 1.2 cm in most runs. The apparatus included an Arenberg PG-650C pulsed oscillator, the receiving section of a Matec 900 attenuation comparator, and a Matec 2470 attenuation recorder which was operated in either the single- or multiple-echo mode. The temperature of the samples was monitored by a thermocouple and recorded on the same plot as the attenuation; it could be regulated to within 0.05°C by circulating water from a constant-temperature bath through a jacket enveloping the cell. The temperature of the bath was controlled thermostatically by two heating elements and a cooling system consisting of a tubular coil connected to a liquid-air supply. The samples, supplied by Eastman Organic Chemicals, were surrounded by an inert atmosphere in the course of the experiments in order to reduce contamination, which has the effect of shifting the transition temperature. For the same reason, fresh samples were used in each experimental run.

Figure 1 shows typical data of the ultrasonic attenuation α_0 as a function of $T - T_0$, where T_0 is the temperature at which the attenuation reaches a maximum value. Since T_0 and T_c, the temperature of the transition, may be different, we prefer to indicate them by different symbols; the measurements we have made cannot be used to establish this difference. These data represent measurements taken on four samples, in the absence of an externally applied magnetic field. The temperature of the peak was slightly different in the various samples, ranging from 40.7 to 41.7°C, probably a consequence of variations in the small amount of impurities introduced while each sample was in use (all samples were part of the same lot, hence presumably their initial purity was the same). It is important to note that, aside from this temperature shift, the curves obtained in the various samples are identical, within the experimental error (about 5%). This observation applies also to the measurements of attenuation in the magnetic field and to the velocity measurements to be described later.[4] The

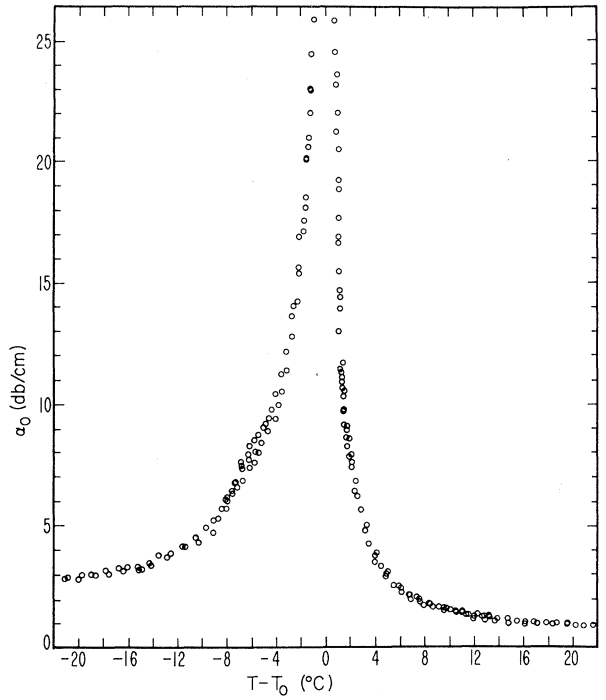

FIG. 1. Ultrasonic attenuation versus temperature at $f = 3.5$ MHz. T_0 is the temperature of maximum attenuation, about 41°C in MBBA.

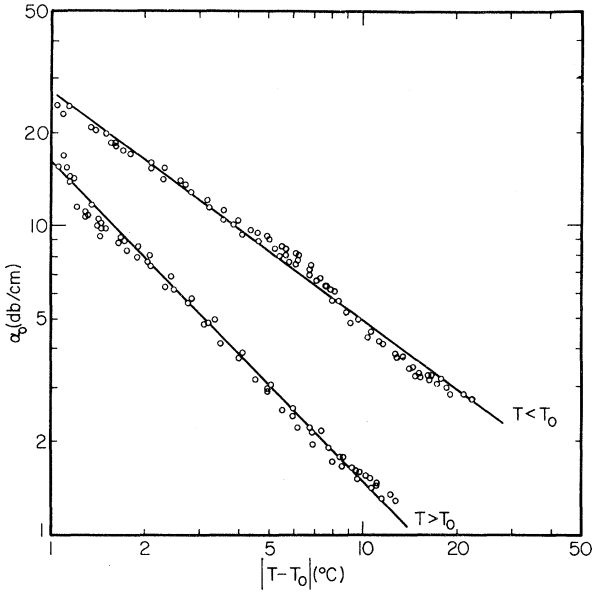

FIG. 2. Ultrasonic attenuation versus temperature at $f = 3.5$ MHz. The solid lines represent least-squares fits of the form $\alpha_0 = a|T - T_0|^{-b}$.

diffraction correction was found to be negligible. The corresponding values of α_0/f^2 are consistent with the measurements made by Candau and Martinoty[5] at selected temperatures and above 15 MHz; the present data can be used to extend on the low-frequency side the computation of their curves based on the assumption of a single relaxation process.

The same data are presented on a logarithmic scale in Fig. 2, together with least-squares–fitted power curves of the form $\alpha_0 = a|T - T_0|^{-b}$, where for $T < T_0$, $a = 27.69$ and $b = 0.75$, while for $T > T_0$, $a = 16.33$ and $b = 1.04$. In both regions the value of the correlation coefficient is 0.99.

The procedure adopted for the attenuation measurements in the presence of applied magnetic fields was the following: The sample was initially heated to a temperature far above the transition temperature (typically, up to about 65°C); then the field was turned on. The attenuation measurements were made as the temperature was subsequently decreased in small steps from the isotropic to the nematic phase. The data presented here were obtained with fields of 500 G; several auxiliary experiments, which were performed in order to determine the value of the fields sufficient to obtain saturation conditions, yielded the same results in fields up to 2500 G.

It was noted that upon turning off the magnetic field while the sample was in the nematic phase, the value of the zero-field attenuation was recovered after a time which was strongly dependent on the temperature; typically, this time varied from about 50 sec at 40°C to about 750 sec at 25°C, and it could be decreased considerably by mechanical agitation of the sample. The time required for the inverse process (i.e., for the value of the attenuation to undergo the full change upon turning on the field) was approximately temperature independent and of the order of 50 sec.

The results of these measurements are displayed in Fig. 3 which shows the differences between the zero-field attenuation α_0, and the attenuations in longitudinal and transverse fields $\alpha_\parallel$ and $\alpha_\perp$, respectively, as functions of temperature; the curves in this figure are best fits to the experimental data. The difference between $\alpha_\parallel$ and $\alpha_\perp$ is also shown, and it presents a marked temperature dependence in the vicinity of T_0. To our knowledge, this effect has not been reported before; however, a careful examination of the curves obtained by Kemp and Letcher in PAA and PAP suggests a similar behavior, if extended toward the transition temperature. Our value of $\alpha_\parallel - \alpha_\perp = 0.9$ dB/cm at $T = 22°$ C is within 25% of the result obtained by Lord

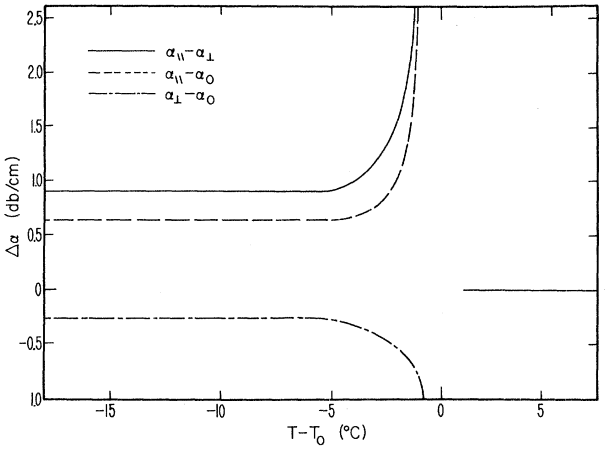

FIG. 3. Differential ultrasonic attenuation versus temperature at $f = 3.5$ MHz. α_0 is the attenuation in zero magnetic field; $\alpha_{\parallel}$ and $\alpha_{\perp}$ are attenuations in 500-G longitudinal and transverse magnetic fields, respectively.

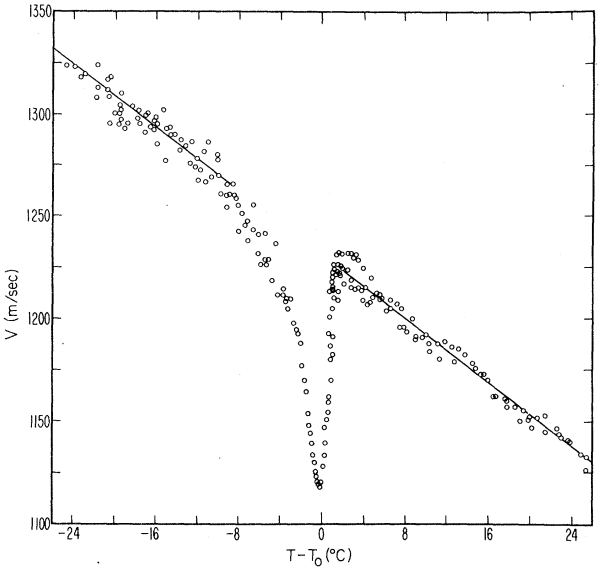

FIG. 4. Velocity of longitudinal waves at $f = 3.5$ MHz versus temperature.

and Labes at the same frequency and at room temperature. It is of interest to note that from our data we obtain the relation $\alpha_0 = (0.33 \pm 0.04)\alpha_{\parallel} + (0.67 \pm 0.04)\alpha_{\perp}$, valid for $-17°C < T - T_0 < -1.5°$ C. This result is consistent with the assumption that ordered regions within the sample are randomly oriented in zero magnetic field; the only effect of the field is to modify this configuration.

In the isotropic phase, no field dependence of the attenuation was observed within the accuracy of the measurements (about 5%).

Figure 4 shows the ultrasonic velocity at a frequency of 3.5 MHz as a function of temperature. The velocity was determined by measuring the time of flight of the pulses; the estimated accuracy of these measurements is about 1%. Within this limit, no influence of the magnetic fields was observed.

The straight lines drawn through the experimental points were obtained by least-square fits to the data in the temperature ranges $T - T_0 < -8°C$ and $T - T_0 > 2°C$. The slope was -3.57 for $T < T_0$ and -3.98 for $T > T_0$. In the transition region the velocity decreased sharply by about 9% to a minimum value of 1118 m/sec. The temperature dependence of the velocity in this region has been discussed recently by Kapustin and Mart'yanova[6] on the basis of the molecular statistical theory.[7,8] It should be of interest to relate the present measurements to that theory when the various parameters necessary for the calculations become available for MBBA.

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