SOME PROPERTIES OF LIQUID CRYSTALS

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The present paper contains the results of measuring the velocity and absorption of ultrasonic waves in materials of the homologous series of dialkoxyazoxybenzenes. The existence of pretransition states in liquid-mesophase and mesophase-mesophase temperature transitions was detected for the first time. Regular fluctuations of the velocity and absorption were noted. The ferroelectric properties of the nematic and smectic phases of para-nor-mal octoxybenzoic acid (domains, hysteresis effects) were discovered. Experimental data on the scattering of light by cholesteric-type liquid crystals and their mixtures were obtained, it is shown that the sequence and rate of change of specimen color depend strictly on temperature.

The liquid crystalline phase (mesophase) resembles the ordinary liquid phase in being fluid, but differs from the latter in the anisotropy of its optical and other properties. For example, liquid crystal molecules exhibit marked electrical and magnetic anisotropy. The explanation of the mesophase lies in the morphological structure of the molecules, which encourages selective relative orientation. Mesophases of pure materials can exist only in a specific temperature range whose limits vary negligibly with pressure in accordance with the Claparion–Clausius equation. At higher temperatures the material becomes an isotropic liquid; at lower temperatures it consists of solid crystals.

Liquid crystals have smectic, nematic, and cholesteric mesophases. One of the characteristic properties of liquid crystals is the parallel disposition of rod-shaped molecules within certain microregions (domains).

A given compound usually has one, at most two, mesophases. The phase transitions accompanying changes in temperature occur as follows:

\[ T_1 \rightarrow T_2 \rightarrow T_3 \rightarrow T_4, \]

solid smectic nematic isotropic phase liquid

the temperatures \( T_1, T_2, T_3, T_4 \) are reproducible, and \( T_2, T_3 \) are readily reversible. However, Wiegend found an n-octoxybenzal (p-propylaniline) which exhibits four liquid crystalline states (polymesomorphism). The ordering of molecules in the material is different in each of these states.

The formation, structure, and properties of liquid crystals have received very little attention. The accumulation of experimental data to form the basis of a future theory of the phenomenon is a fundamental task. Our immediate purpose, however, is to investigate the phase transition mechanism, the size of the molecular domains, the character of the boundaries between these domains, and other facets of the problem in relation to time, external forces, temperature, etc. We note once again that the pliability of liquid crystals and the fact that their structure can be altered by applying various external forces are certain to make them useful in various technical applications.

PHASE TRANSITIONS IN LIQUID CRYSTALS

Our study of phase transitions brought to light many interesting but apparently contradictory facts. Specifically, one of the properties of liquid crystals (optical anisotropy) testifies to molecular ordering. On the other hand, X-ray photographs do not reveal or reveal only slight changes at the transition point (in the absence of sufficient orienting forces). This means that transitions involve almost no abrupt changes in the disposition of molecules. At the same time, we detected a definite, though quite small, heat of transformation. Density measurements revealed a small jump (of about 1%). The viscosity has a maximum in the neighborhood of the transition point.

Of special interest are phase transitions in those materials which have several mesomorphic states. Changes in the temperature of these substances are accompanied by a steady growth of the degree of molecular ordering as the isotropic liquid becomes a solid crystal. This opens up the possibility of studying the intermediate stages of reorganization from the isotropic to the solid state.

Polymesomorphic materials are also interesting because, owing to the small heat of transformation, they can be expected to exhibit marked pretransition effects.

Experience shows that ultrasonic techniques are one of the most effective means of studying the nature of temperature-dependent transitions in liquid crystals.

Measurements over a broad range of temperatures (including the phase transition range) have already been made of the velocity and absorption of ultrasound in various types of liquid crystals: parazazoxyanisol, parazazoxyphenetol, cholesterlybenzoate, and \( p^l \)-non-axybenzaloluidine [1]. These early results enabled us to conclude that regardless of the nature of the material, the velocity of sound has a minimum, and the absorption coefficient a maximum, near the phase transition point.
An entirely new and very interesting problem in the study of intermediate states in liquid crystals is whether pretransition states occur in each transition (isotropic liquid → mesophase, mesophase → mesophase, mesophase → solid). The possibility of such pretransition states is quite plausible physically, but there has been no careful verification of their existence. To study this question the present author and Bykova investigated velocity and absorption in two members of the homologous series: para-normal heptyloxybenzoic acid and para-normal octyloxybenzoic acid. Both of these compounds exhibit smectic and nematic states. The absorption and velocity of ultrasound are shown as functions of temperature in Figs. 1 and 2. We see that the absorption maximum in the mesophase-mesophase range is approximately seven times smaller than the isotropic liquid-mesophase range. The ratio $a/v^2$ was found to decrease with increasing frequency. Stokes' law $a/v^2 = \text{const}$ held for the isotropic liquid at a temperature $5^\circ$ above the transition point. Absorption in the smectic state was of the same order as that in the isotropic liquid. The experimental results therefore confirmed all expectations: an absorption maximum and a velocity minimum were noted both in the isotropic liquid-mesophase and in the mesophase-mesophase ranges. As regards the mesophase-solid crystal range, we are not yet able to give an answer: the experiment required was quite complicated and was not, in fact, performed.

Figure 2 shows the behavior of ultrasound in the neighborhood of the phase transition temperatures. The experimental curves can be explained on the basis of the structural changes occurring in the material. We know that the velocity and absorption of sound are related to molecular structure, to the intensity and character of molecular interaction, and to the possible molecular structure of the material as a whole. In an isotropic liquid of decreasing temperature the velocity first increases linearly and then diminishes, reaching a minimum near the transition point. The abrupt decrease in the velocity of sound near the isotropic-nematic transition is apparently attributable to the fact that the pretransition state of the material is unstable, which results in increased compressibility and a concomitant decrease in the velocity.

The increase in velocity after the minimum is due to other factors and has to do with the change in the degree of ordering of the molecule of the nematic mesophase [2]. The velocity again passes through a minimum in the neighborhood of the nematic-smectic transition.

In the smectic mesophase the velocity once again increases with decreasing temperature as a result of structural changes which bring the material closer to the solid state. The ultrasound velocity was also found to depend on frequency. For an isotherm in the isotropic-nematic transition range of para-normal heptyloxybenzoic acid the dispersion at the frequencies 3.1 Mc and 15 Mc turned out to be 5.8%; the dispersion at the nematic-smectic transition was 0.8%. Qualitatively similar results were obtained for the second homolog.

Mart'yanova studied the behavior of the velocity and absorption for six members of the homologous series of dialkoxyazoxybenzene. She detected pretransition states for all members of the series, and observed for the first time the regular fluctuations of the absorption and velocity which are apparently attributable to changes in the number of carbon atoms.

![Figure 3. Domain structure in various portions of a paraazoxyphene-tol preparation in a pulsed field. Crossed Nicol prisms. Magnification 5 x 8. Layer thickness d = 0.002 cm. Pulse duration 2 msec; pulse repetition rate 150 cps; amplitude 20 V.]