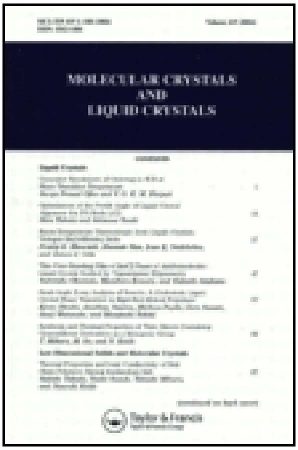

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Ultrasonic Behaviour of Mixed Liquid Crystals near Phase Transition

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Investigations of ultrasonic velocity (V), density (ρ), adiabatic compressibility (β_{ad}), molar sound velocity (R) and ultrasonic absorption ($\alpha\lambda$) are carried out in two types of mixed liquid crystals—namely, *p*-azoxyanisole-azoxybenzene, and cholesterol-cetyl alcohol. The former exhibits a nematic mesophase and the latter exhibits a smectic mesophase throughout their isotropic and anisotropic phases at different concentrations. Abrupt jumps in the parameters, V, β_{ad}, R and $\alpha\lambda$ are observed in the vicinity of the isotropic-mesophase transition in these liquid crystalline mixtures, while the density exhibited linear variation. The abrupt jumps in the parameters, V, β_{ad}, R and $\alpha\lambda$ are found to decrease with increase of concentration of the non-mesomorphic compound in the *p*-azoxyanisole mixture, while they are found to increase with increase of cholesterol concentration in the cholesterol-cetyl alcohol mixture. It is tentatively concluded that in the former mixer the mesomorphic property has decreased, while in the latter it has increased with the addition of a foreign compound. The temperature variation of the order parameter S is estimated in the *p*-azoxyanisole mixture from compressibility data. As the ultrasonic behaviour of the *p*-azoxyanisole-azoxybenzene mixed liquid crystals at the phase transition has been found to have distinct similarities with that of critical solutions at critical solution temperature, the experimental data of $\alpha\lambda$ has been fitted with Fixman's theory of critical solutions and the agreement has been found to be satisfactory.

INTRODUCTION

Study of mixed liquid crystals is of particular interest as it gives considerable insight about the mesomorphic state of the liquid crystalline compound and the variation of the mesomorphic state when a foreign impurity is added. Liquid crystals are characterised by high molecular orientational order in their mesomorphic state and if any non-mesomorphic compound is dissolved in it, the molecular orderliness should be affected and hence the physical properties, such as density, ultrasonic velocity, absorption, viscosity and consequently, it will be interesting to study the behaviour of ultrasonic velocity, density, adiabatic compressibility and other parameters near the phase transition of mixed liquid crystals, varying the concentration of the foreign compound.

Among liquid crystals, the nematic state is widely investigated both theoretically and experimentally. In the nematic phase the lateral, planar and terminal intermolecular attractions existing between molecules are sufficiently strong to keep the molecules intact in their ordered structure characteristics of the nematic phase. With the addition of a foreign impurity these lateral, planar and terminal attractions will decrease and this decrease will continue with the increasing concentration of a foreign substance and ultimately beyond a particular concentration, these lateral planar and terminal attractions would become sufficiently weak enough to allow the molecules to move freely from their ordered structure to give the disordered isotropic liquid. It is of special interest to study the ultrasonic properties in such liquid crystalline mixtures.

The mixed liquid crystal systems can be generally classified as follows:-

a) Where both the components are liquid crystalline substances,

b) Where one component is a liquid crystal and the other non-liquid crystal and

c) Where both the components are non-liquid crystalline substances.

The effect of addition of foreign substances on mesomorphic structure has been discussed by Gaubert.[1] Liquid crystallinity in mixtures of two non-mesomorphic substances have been reported by Mlodziejowski,[2] Gaubert[3] and Kravchenkov and Pastukova.[4] The extent of the melting point depression and the phase diagrams for some liquid crystalline mixtures are well illustrated and discussed by Tamman,[5] Lehmann[6] and others. Friedel[7] has made many interesting observations on the effects on the textures of various mesophases with the addition of other mesomorphic compounds. Except the above said work practically no work appears to have been done on the study of the physical properties such as density, viscosity, specific heats, etc. In view of the scarcity of the work done on liquid crystalline mixtures the present problem of investigating ultrasonic velocity, density, absorption and other related parameters was chosen by the authors.

EXPERIMENTAL DETAILS

1 Preparation of mixtures

The two liquid crystalline mixtures chosen for investigation are (a) *p*-azoxyanisole + azoxybenzene and (b) cetyl alcohol + cholesterol; the former consists of a mesomorphic and a non-mesomorphic compound while the latter consists of two non-mesomorphic compounds. The chemicals *p*-azoxyanisole, azoxybenzene, cholesterol, and cetyl alcohol were obtained from Messrs. B. D. H. Chemicals, England.

The two substances comprising the mixture are accurately weighed in the required proportion in a test tube using a Mettler microbalance. The mixture in the test tube is placed in a temperature bath and heated to a temperature slightly higher than that at which the mixture melts. When the mixture is melted, it is thoroughly stirred by means of a glass rod in order to ensure thorough and complete mixing of the respective components. This homogeneous liquid is then quickly cooled and solidified by quenching the substance, keeping the test tube in a beaker containing ice. The solid is removed from the test tube and ground to a fine powder using an agate mortar. Again the mixture is heated to a temperature above its melting point, and is then suddenly quenched and ground to a fine powder. This procedure is repeated until the transition temperature and melting point reach constant values. Both of the mixtures of *p*-azoxyanisole + azoxybenzene and cetyl alcohol + cholesterol are prepared following the above procedure. The melting points and transition points are determined by an optical method using a polarising microscope and they are compared with the values given by Dave and Dewar.[8]

2 Measurement of ultrasonic velocity, density and absorption

The velocity measurements are carried out with a fixed path double crystal interferometer at a frequency of 2 Mc/s. The densities are determined using a special dilatometer constructed for this purpose. The details of the experimental set up used for velocity measurements and the special dilatometer used for density measurements are already described in an earlier communication.[9] The velocity measurements are accurate to 1 m/sec and the densities are accurate to 0.0001 g/cm.^{3} The temperature is controlled to 0.1° C in these measurements and it is measured by a calibrated chromel-alumel thermocouple, using a potentiometer. The absorption measurements are carried out at three frequencies of 3, 5 and 9 Mc/s using a pulse technique. A pulsed R. F. Oscillator supplies R. F. pulses to a x-cut quartz crystal, and another identical quartz crystal is mounted on a precision micrometer screw with a least count of 0.0005 cm and acts as a receiver for the ultrasonic pulses travelling through the liquid medium.

The transmitting crystal is attached to a fused quartz rod of 5 cm length, which is pierced through the bottom of the ultrasonic cell container, while another fused quartz rod of 10 cm length, to which the receiving crystal is attached, is inserted from the top of the cell. The receiving crystal attached to the micrometer screw moves along a vertical axis while the transmitting crystal is aligned to this direction by adjusting the proper levelling screws. The R.F. output from the receiving transducer is fed to 30 Mc/s I. F. amplifier, after preamplification through a converter. Detected vedeo pulses from this amplifier are fed to a Dumont type 256F oscilloscope where the pulse pattern is obtained. A piston attenuator provided in the receiving channel is used to measure the absorption coefficient to 0.1 db. The ultrasonic cell is a double walled container, containing an inlet and outlet for circulating paraffin oil. The paraffin oil from a tank maintained at a constant temperature by a thermostat is circulated through the ultrasonic cell and is again pumped back to the tank by using a motor vacuum pump. The temperature of the liquid crystal specimen in the ultrasonic cell is controlled to ±0.2° C. The absorption measurements are accurate to 5 to 8 %.

3 Presentation of Results

The following mixtures and the components of those mixtures were investigated

1) *p*-Azoxyanisole
2) Azoxybenzene
3) 96 % *p*-Azoxyanisole + 4 % Azoxybenzene
4) 94 % *p*-Azoxyanisole + 6 % Azoxybenzene
5) Cetyl alcohol
6) 10 % Cetyl alcohol + 90 % Cholesterol
7) 15 % Cetyl alcohol + 85 % Cholesterol
8) 30 % Cetyl alcohol + 70 % Cholesterol.

The velocity, density and absorption measurements were carried out throughout the anisotropic region and 10°C to 15°C beyond the phase transition of every mixture and of *p*-azoxyanisole, and at their phase transitions, paying special attention to the measurements at the phase transitions. Though the measurements are also carried out in cetyl alcohol and azoxybenzene they are not carried out in cholesterol as it has a high melting point and is very susceptible to oxidation. The ultrasonic velocities, densities and absorption are reported for the first time in all the compounds except in *p*-azoxyanisole. The parameters, adiabatic compressibility (β_{ad}), molar sound velocity (R), molar compressibility (B), are estimated using the following relations

$$\beta_{ad} = \frac{1}{\rho V^2}, \; R = \frac{M}{\rho} V^{1/3}, \; B = \frac{M}{\rho} \frac{1}{\beta_{ad}^{1/7}}$$

where ρ is the density, V is the ultrasonic velocity and M is the molecular weight.

The results of V, ρ, β_{ad} for *p*-azoxyanisole, for azoxybenzene and for the mixtures are presented in Figures 1 and 2, and R values are presented in Figure 3. The results of V, ρ, β_{ad} for cetyl alcohol and for the cetyl alcohol cholesterol mixtures are presented in Figures 4 and 5, and the R values are presented in Figure 6. The variation of order parameters S with $T_c - T$ is

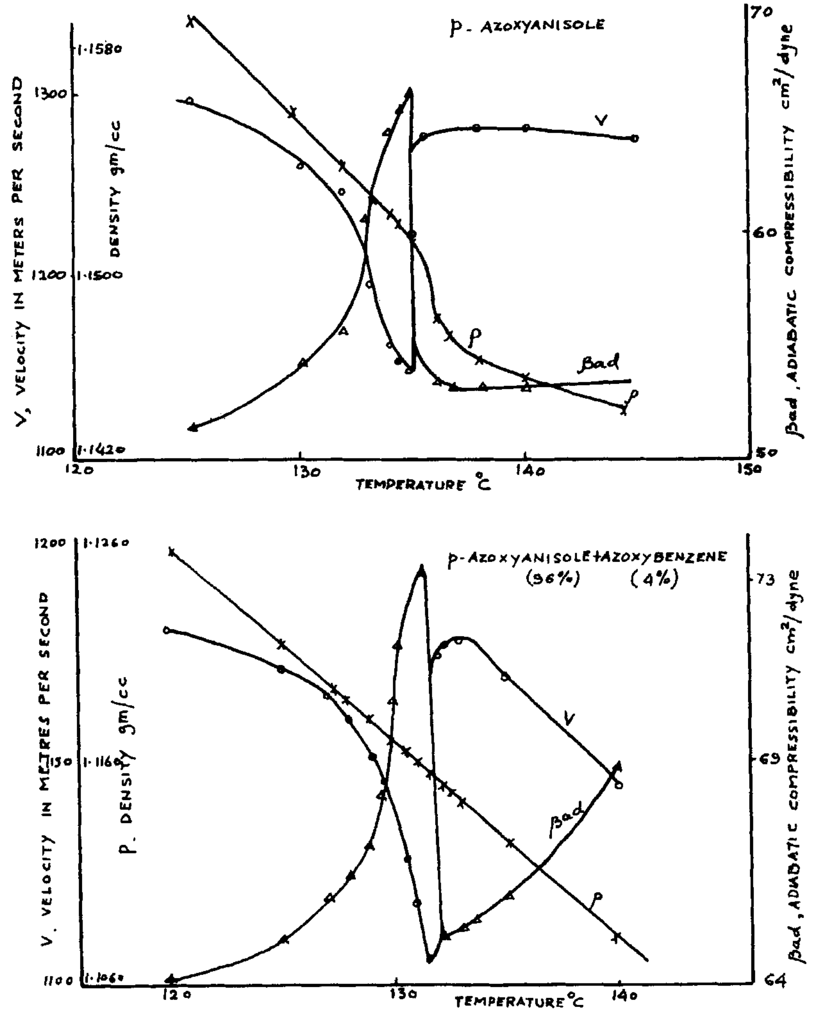

FIGURE 1 Temperature variation of ultrasonic velocity density and adiabatic compressibility in *p*-azoxyanisole and *p*-azoxyanisole (96%) + azoxybenzene (4%).

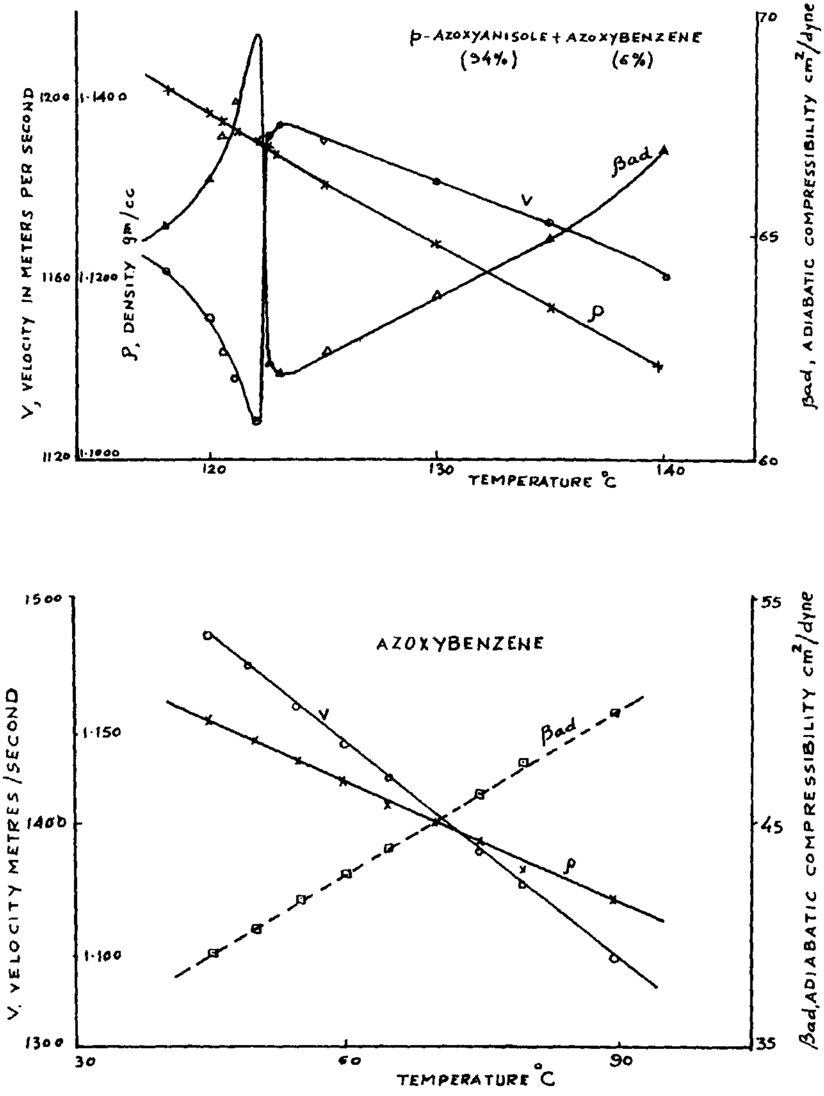

FIGURE 2 Temperature variation of ultrasonic velocity, density and adiabatic compressibility in azoxybenzene and *p*-azoxyanisole (94%) + azoxybenzene (6%).

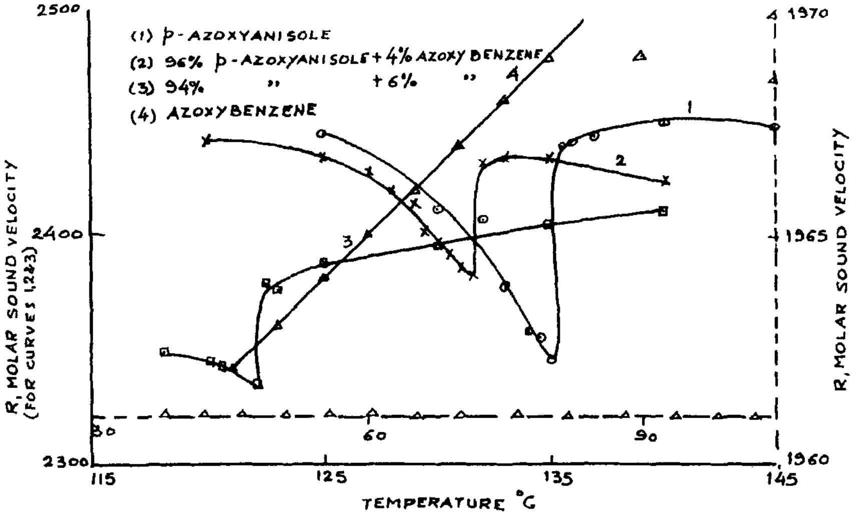

FIGURE 3 Temperature variation of molar sound velocity in *p*-azoxyanisole, azoxybenzene, *p*-azoxyanisole (96%) + azoxybenzene (4%) and *p*-azoxyanisole (94%) + azoxybenzene (6%).

plotted in Figure 7. The absorption values of α/f^2 for *p*-azoxyanisole and its mixtures are presented in Figure 8, while the results of α/f^2 for cholesterol-cetyl alcohol mixtures are presented in Figure 9.

DISCUSSION

Variation of V, ρ, β_{ad} and R in mixtures of paraazoxyanisole + Azoxybenzene

The variation of velocity (V), density (ρ) and adiabatic compressibility (β_{ad}) for the *p*-azoxyanisole-azoxybenzene mixtures and the pure compounds *p*-azoxyanisole and azoxybenzene are presented in Figures 1 and 2. A study of the figures shows that the variation of ultrasonic velocity with temperature in the mixture is similar to the anomalous behaviour observed in *p*-azoxyanisole. In both the mixtures and in *p*-azoxyanisole the velocity shows an abrupt minimum at the phase transition and far away from the transition it varies linearly in the isotropic phase, while it is non-linear in the anisotropic phase. The density variation shows perfect linearity in the mixtures unlike in *p*-azoxyanisole and the adiabatic compressibility shows an abrupt jump at the phase transition. From a study of Figures 1 and 2 it is interesting to note that the velocity dips and the adiabatic compressibility jumps have decreased in going from pure *p*-azoxyanisole to the mixtures. This behaviour

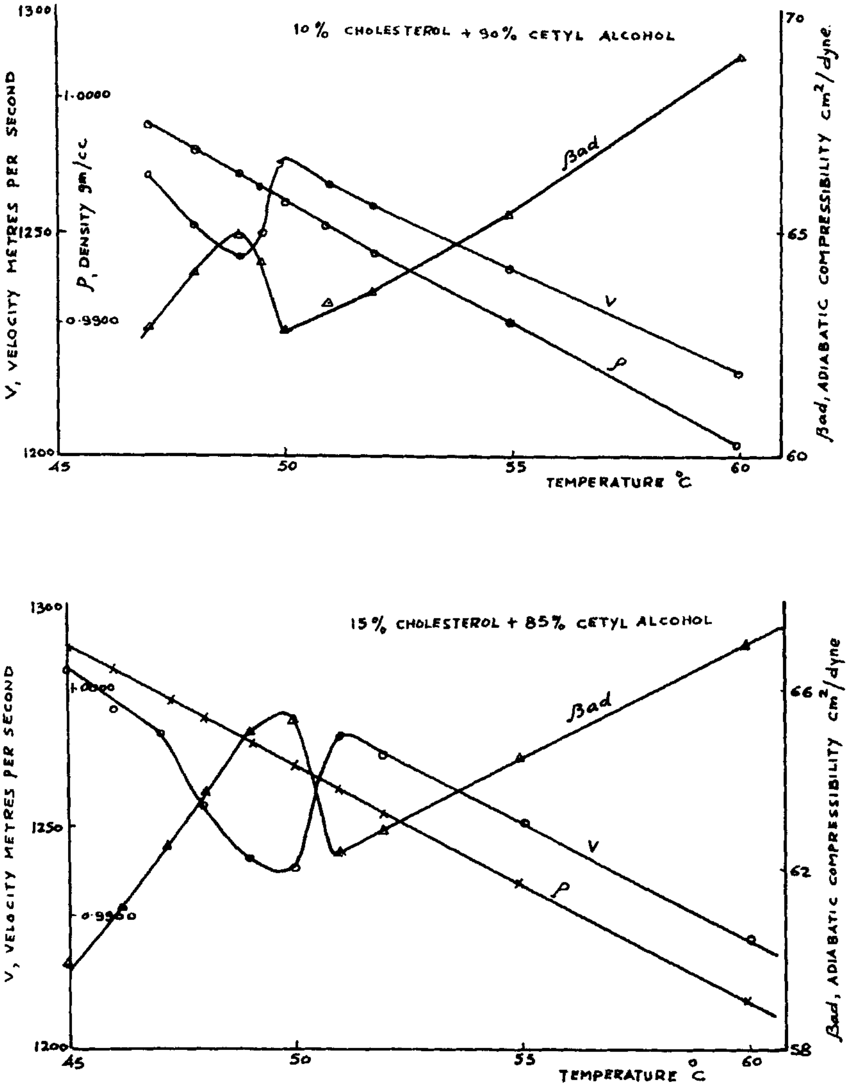

FIGURE 4 Temperature variation of ultrasonic velocity, density and adiabatic compressibility in cetyl alcohol (90%) + cholesterol (10%) and cetyl alcohol (85%) + cholesterol (15%).

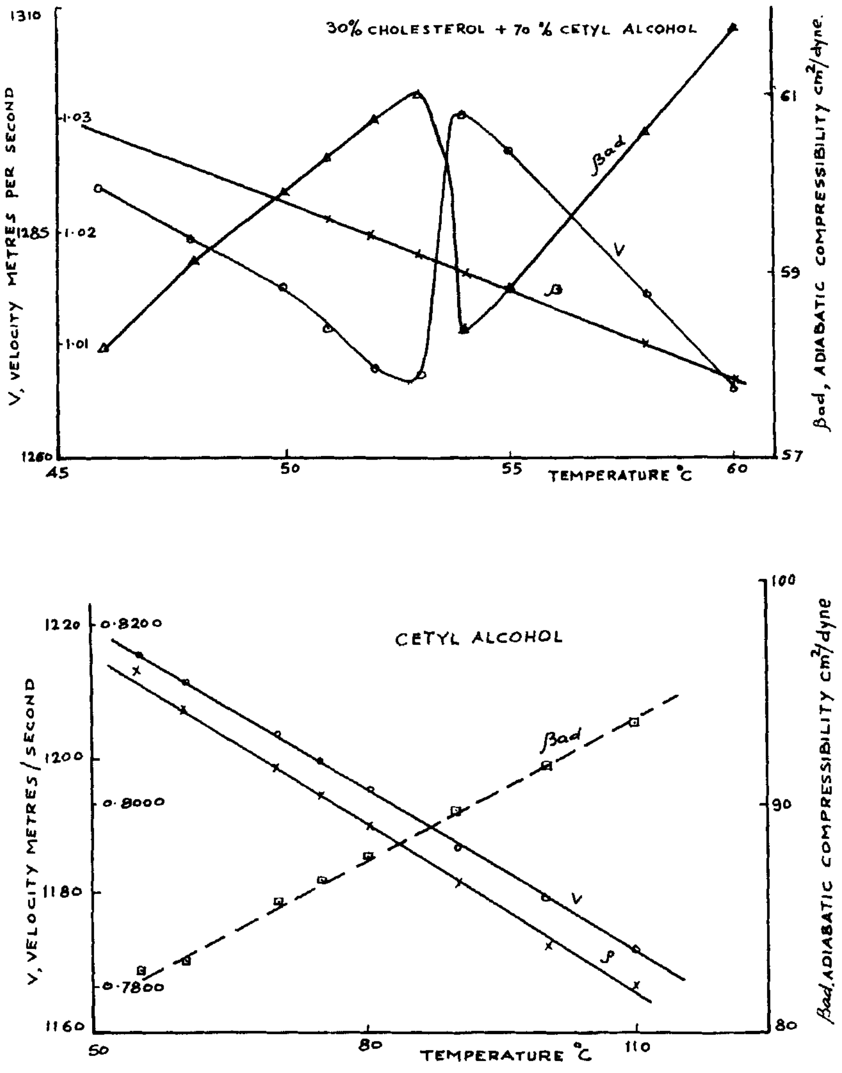

FIGURE 5 Temperature variation of ultrasonic velocity, density and adiabatic compressibility in cetyl alcohol (70%) + cholesterol (30%) and cetyl alcohol.

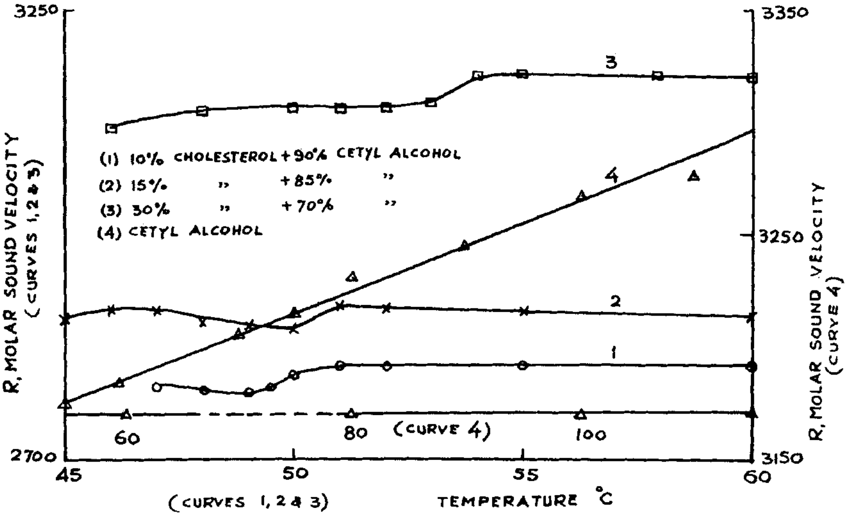

FIGURE 6 Temperature variation of molar sound velocity in cetyl alcohol and mixtures of cholesterol and cetyl alcohol.

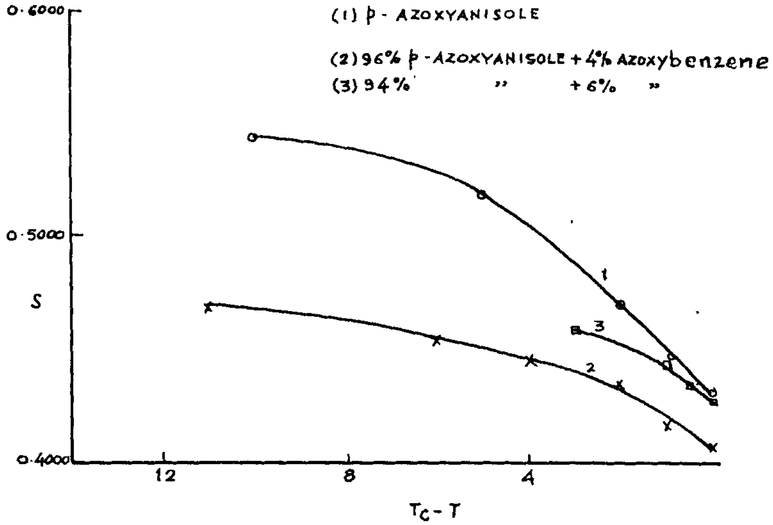

FIGURE 7 Plots of $T_c - T$ versus order parameter S.

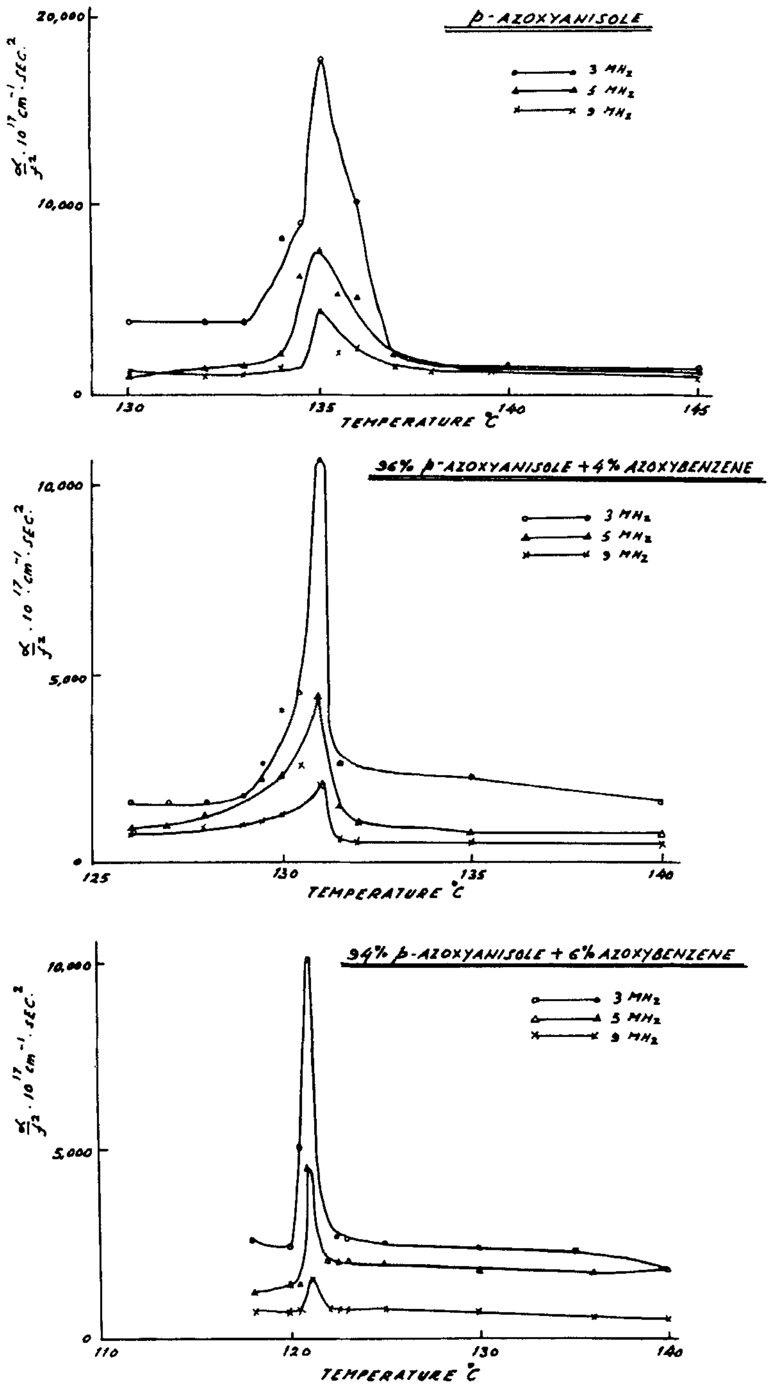

FIGURE 8 Temperature variation of α/f^2 in p-azoxyanisole and mixtures of p-azoxyanisole and azoxybenzene.

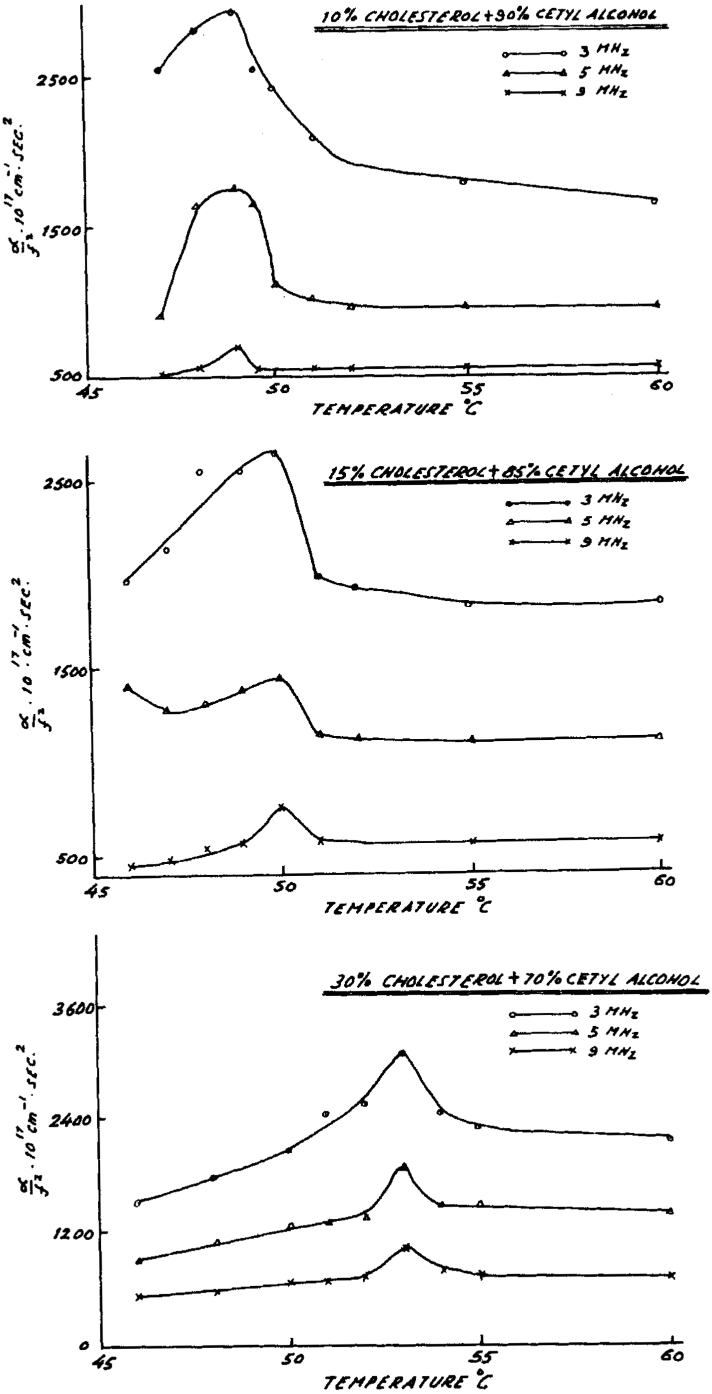

FIGURE 9 Temperature variation of α/f^2 in mixtures of cetyl alcohol and cholesterol.

indicates that with increase in concentration of nonmesomorphic compound, the nematic state of the liquid crystal *p*-azoxyanisole begins to show disruption. The velocity and density varies linearly with temperature in azoxybenzene; the same is observed with the adiabatic compressibility and the molar sound velocity.

The nature of the variation of molar sound velocity in *p*-azoxyanisole, azoxybenzene and the two mixtures is presented in Figure 3. From a study of the figure, it is evident that the molar sound velocity in both the mixtures shows a slight variation with temperature in the isotropic phases just like in the parent liquid crystal compound *p*-azoxyanisole. At the isotropic-mesophase transition the molar sound velocity shows an abrupt drop and after crossing the transition point the molar sound velocity shows a regular increase though not linear. The remarkable feature is that away from the transition in the isotropic phase and in the mesophase, R is nearly independent of temperature. The molar compressibility is found to vary in a similar way to that of R.

Variation of V, ρ, β_{ad} and R in cetyl alcohol + cholesterol mixtures

Although cholesterol is nonmesomorphic, it is considered to be potentially mesomorphic since even cholesteryl chloride gives a monotropic cholesteric mesophase, the non-mesomorphic property of cholesterol is due to the presence of hydrogen bonding which increases the inter-molecular cohesion and hence the melting point. The presence of cetyl alcohol molecules may provide alternative sites to which the cholesteryl hydroxyl group can, hydrogen bond without resulting in a high melting crystal lattice, yet giving sufficiently strong intermolecular attractions to make possible the existence of an anisotropic melt.

It has been found from birefringence measurements that cetyl alcohol + cholesterol gives rise to a smectic mixture and the liquid crystalline property increases with increasing concentration of cholesterol. The temperature variation of ultrasonic velocity (V), density (ρ), adiabatic compressibility (β_{ad}) and molar sound velocity (R) in three different concentrations of the above mixture and pure cetyl alcohol are presented in Figures 4, 5, and 6. In pure cetyl alcohol which is a non-mesomorphic compound the velocity and density increases linearly with decrease of temperature as is characteristic of most of the ordinary organic liquids; correspondingly, the β_{ad} and molar sound velocity are also linear (Figures 5 and 6). In all three mixtures the V and R values show broad minima and β_{ad} shows maxima though the densities are linear (Figures 4, 5, and 6). A study of the results indicates that the magnitude of the minima in the velocity and the molar sound velocity and maxima in β_{ad} increases with increasing additions of cetyl alcohol.

It can be concluded from these results that ultrasonic behaviour can be correlated to the liquid crystalline property of these mixtures.

Variation of order parameter S in p-azoxyanisole mixtures

The changes observed in ultrasonic parameters V, β_{ad} and R can obviously be correlated with the change in mesomorphic state of the liquid crystalline mixture. The mixtures should have less degree of order than the parent compound, and the degree of order decreases with increasing concentration of the non-mesomorphic compound. Ultimately beyond a certain concentration of the non-mesomorphic compound, the degree of the order should vanish completely and the mixture should behave like an isotropic liquid.

The degree of orientational order in a nematic liquid crystal is defined by an order parameter S as given by Maier and Saupe[10]

$$S = \tfrac{1}{2}(3\,\overline{\cos^2\theta} - 1) \tag{1}$$

where θ is angle between the long axis of a molecule and the axis of preferred orientation which coincides with the symmetry-axis, in uniformly oriented nematic liquids. They also found that for all nematic liquids the order parameter reaches the limiting value of 0.44 at the transition temperature. It is expected that the addition of a non-mesomorphic compound like azoxybenzene, to p-azoxyanisole should reduce considerably, the order parameter S. An attempt is made here to estimate the change in the order parameter S with the addition of non-mesomorphic compound from ultrasonic velocity and density data and with the formula proposed by Chandrasekhar and others,[11] making some assumptions. Chandrasekhar and workers supposed that in the nematic state the molecules may be expected to execute rotational oscillations or librations about the mean orientation, assuming the well-known relation of the Einstein model as

$$\Theta \propto \rho^{1/3} V$$

where Θ is the Einstein characteristic temperature, ρ is the density, and V is the ultrasonic velocity. Cruickshank[12] showed that when $T \gg \Theta$ the mean square libration amplitude $\overline{\theta^2}$ can be written as

$$\overline{\theta^2} \propto T\rho^{-2/3}V^{-2} \tag{2}$$

or

$$\overline{\theta^2} = kT\rho^{-2/3}V^{-2} \tag{3}$$

where T is the absolute temperature and k is a constant.

Chandrasekhar and others[11] showed that this result though necessarily approximate enables one to make a rough estimate of the variation of the librational amplitude with temperature, from the available ultrasonic velocity data. They showed further that for rotational oscillation

$$S = \tfrac{1}{2}\cos^2(\sqrt{2}\,\theta_{\mathrm{rms}}) + \cos(\sqrt{2}\,\theta_{\mathrm{rms}}) \tag{4}$$

where $\theta_{\mathrm{rms}} = (\overline{\theta^2})^{1/2}$.

From Eqs. 3 and 4, since S_k the order parameter at the transition is known the temperature variation of S is estimated for *p*-azoxyanisole and *p*-azoxyanisole + azoxybenzene mixtures and the results are plotted in Figure 7. Here Eqs. 1, 2, and 3 and the Maier–Saupe rule are used to estimate the variation of the order parameter S of *p*-azoxyanisole with the addition of azoxybenzene and also to study the variation of S with temperature in liquid crystalline mixtures of *p*-azoxyanisole-azoxybenzene. After estimating the libration amplitude from Eq. 4 the value of the constant k in Eq. 3 is evaluated from the density and ultrasonic velocity data. It is assumed that k is independent of the nature and concentration of the non-mesomorphic compound present in *p*-azoxyanisole for small concentration changes and also independent of temperature. The k value obtained from the ultrasonic velocity data of *p*-azoxyanisole is used in estimating the libration amplitude in the mixtures and in turn θ and S values. Using this S value, the variation of S with temperature is estimated in the mixture from the ultrasonic velocity and density data. The results are presented in Figure 7. A study of the results indicates that the variation of S with temperature is more rapid in pure *p*-azoxyanisole than in mixtures.

Variation of absorption in *p*-azoxyanisole mixtures and cetyl alcohol mixtures

Figure 8 represents the variation of α/f^2 with temperature in *p*-azoxyanisole, 96% *p*-azoxyanisole + 4% azoxybenzene and 94% *p*-azoxyanisole + 6% azoxybenzene mixtures throughout their isotropic and anisotropic phases at frequencies of 3, 5, and 9 MHz. A glance at the figures reveals that α/f^2 remains constant away from the transition in the isotropic and anisotropic phases, but exhibits a maximum at the phase transition in all the mixtures, just like in *p*-azoxyanisole, though the maximum of α/f^2 decreases with increasing additions of azoxybenzene. The same behaviour is observed at all the frequencies of 3, 5, and 9 MHz, though the maximum of α/f^2 at 3 MHz is large compared to the maxima at 5 and 9 MHz, thus indicating the existence of low frequency relaxation. The velocities are also measured at different frequencies of 3, 5, and 9 MHz and the dispersion is found to be negligible.

In Figure 9 we present the variation of α/f^2 with temperature in 90% cetyl alcohol + 10% cholesterol, 85% cetyl alcohol + 15% cholesterol and 70% cetyl alcohol + 30% cholesterol at three frequencies of 3, 5, and 9 MHz, throughout their anisotropic and isotropic phases including the phase transition region. A study of the figures reveals that in these three concentrations the α/f^2 values show broad maxima, and the magnitude and sharpness of the absorption maximum is found to increase with increase of concentration of cholesterol, indicating a definite change in the orientational order of the molecules. The increase of α/f^2 with decrease of frequency indicates the existence in these mixtures of low frequency relaxation. From the above results it can be concluded that with the increasing additions of cholesterol the smectic character of the mixture is increased considerably and it is reflected as an increase in the ultrasonic absorption.

Application of Fixman's theory to *p*-azoxyanisole mixtures

A study of the absorption and velocity results in liquid crystalline mixtures of *p*-azoxyanisole-azoxybenzene shows that the ultrasonic behaviour of these mixtures bear close resemblance to that of thermotropic liquid crystals in the transition region and critical solutions and pure liquids in the critical region. In view of the analogous behaviour exhibited by the liquid crystalline mixtures and the critical solutions, an attempt is made here to test the validity of the Fixman's theory[13] of critical solution in *p*-azoxyanisol-azoxybenzene mixture.

Fixman's theory on sound absorption and velocity in critical solutions is based on a particular relaxation model. Fixman proposed that in the vicinity of the critical solution temperature, vigorous composition fluctuations occur and these are associated with excess entropy. The entropy associated with the long wavelength spectrum of these composition fluctuations in the critical region, is supposed to be strongly coupled with the temperature variations produced by the sound wave and the corresponding energy dissipation occurs resulting in high absorption. He gave the following expression for absorption coefficient as

$$\frac{\alpha}{f^2} = \frac{\pi H}{C_v} \vartheta(d) \tag{5}$$

where

$$d = k^2\left(\frac{h}{\omega}\right)^{1/2} \tag{6}$$

$$H = \frac{\gamma_0 - 1}{4\pi^2} \cdot \frac{R}{C_p^0} \cdot T^2\left(\frac{\partial k^2}{\partial T}\right)^2 \cdot (n_1 + n_2)^{-1}\left(\frac{h}{\omega}\right)^{1/4} \tag{7}$$

$$h = \frac{k_B T}{m_1} \phi_1 V_1^2(n_1 + n_2)(2\pi \beta a C_2)^{-1} \tag{8}$$

where

$\gamma = \frac{C_p^0}{C_v^0}$, C_p^0 is the specific heat in the absence of critical composition fluctuation.

R = gas constant

k_B = Boltzmann's constant

βa, k are the parameters of the long range correlation function, m_i, n_i and c_i are the molecular mass, the number density and the mass fraction of species i, respectively, ϕ is the volume fraction, and V_i is the partial molecular volume, βa is a frictional constant related to the diffusion constant D_{id} of an equivalent mixture by

$$\beta a = \frac{k_B T}{m_2 D_{id}} \tag{9}$$

$\vartheta(d)$ is a definite integral which is known numerically.

Debye has expressed k in terms of simple fluids as

$$k^2 = \frac{6}{l^2} \frac{|T - T_c|}{T_c} \tag{10}$$

where l is the short-range spatial correlation parameter representing the molecular interaction range between two molecules.

Anantharaman *et al*[14] and Singh and worker[15] express Fixman's theory as

$$\frac{\alpha}{f^2} = Af^{-5/4}\vartheta(d) \tag{11}$$

with

$$d = Bf^{-1/2}(T - T_c) \tag{12}$$

where A and B have been evaluated by them from the experimental data.

Taking Eq. 6, where h is given by Eq. 8 in which all the quantities are known except the parameter βa, Fixman while testing the validity of the theory in triethylamine—water mixture, took βa to be 4.05×10^{14}. He has also stated that it will lie generally in the range of 1×10^{13} to 1×10^{15}. Here an attempt has been made to fit the experimental data with Eqs. 6 and 11, by assuming the value of βa to be 2.62×10^{13}. The spatial correlation length l is adjusted to give a best fit with the experimental results. The theoretical values of α/f^2 are estimated in p-azoxyanisole-azoxybenzene mixtures at frequencies of 3 and 9 MHz. The theoretical values of $\alpha\lambda$ are estimated in pure p-azoxyanisole using Fixman's theory of one component fluids at the critical state. The results are plotted in Figure 10.

While applying Fixman's theory to liquid crystalline mixtures it is assumed that vigorous composition fluctuations prevail at the phase transition and these are associated with excess entropy. When ultrasonic waves travel

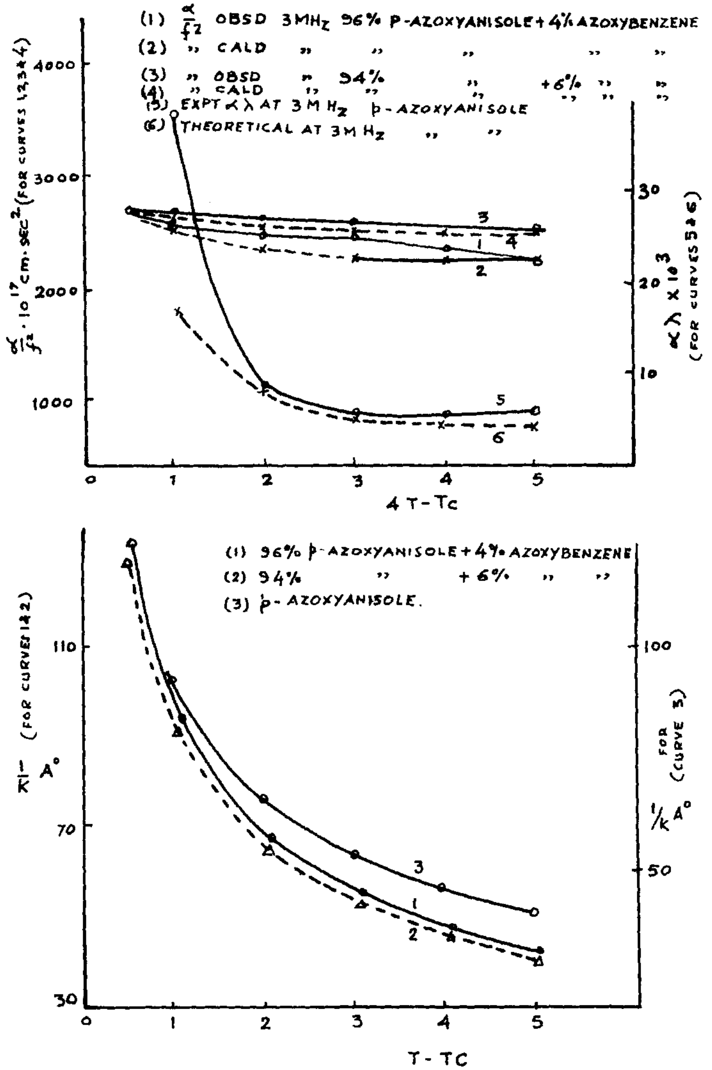

FIGURE 10 Plots of $T_c - T$ versus α/f^2, $\alpha\lambda$ and $1/K$ in p-azoxyanisole and mixtures of p-azoxyanisole and azoxybenzene.

through such a medium the long wave length region of these composition fluctuations strongly interact with the sound wave resulting in high absorption. Since the diffusion of the foreign impurity into the parent compound has considerable effect on the mesomorphic phase transition as it tries to disrupt the nematic order, it is plausible to assume that the untrasonic absorption should also include a diffusion process and also the relaxation processes due to the perturbation of the equilibrium between mesomorphic and non-mesomorphic compounds. A glance at the figures indicates that the estimated values of $(\alpha\lambda)_{\text{theory}}$ and $(\alpha\lambda)_{\text{expt}}$ are in good agreement in *p*-azoxyanisole and also $(\alpha/f^2)_{\text{theory}}$ and $(\alpha/f^2)_{\text{expt}}$ in mixtures. This agreement can be stated to be remarkably satisfactory considering that the above theory has distinct limitations imposed by the approximation used in its developments and by the assumptions which are made upon applying it to liquid crystalline mixtures.

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