

Phase of Thermal-Optical Behavior of Liquid Crystals Mixtures

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ABSTRACT:

We have thermal-optical studies as a function of temperature in liquid crystal. The main contribution to nonlinear optical phenomena in liquid crystals arises from thermal and reorientation processes. While the thermal effect is similar to that observed in other materials, the reorientation effect is characteristic only in liquid crystalline phases. The nonlinearity due to the reorientation effect in nematic phase leads to numerous effects not observed in another types of nonlinearity. The reorientation nonlinearity induces extremely large nonlinear changes of refractive index that can be obtained for relatively low light power. This nonlinearity depends on boundary conditions and geometry of the system and it can be easily modified by external electric or magnetic fields. The nonlinearity depends on light polarization but within a wide range is independent on light wavelengths. The main drawback is slow response time, but by special optimization of the system, this response could be fairly fast.

Key words: thermal-optical, liquid crystal mixture

THERMAL INVESTIGATIONS

Differential scanning calorimetry (DSC) is an important tool in the identification of mesophases and their thermal behaviour. DSC reveals the presence of phase transitions in a material by detecting the enthalpy change associated with each phase transition. The precise identity of the phase (s) cannot be obtained, but the level of enthalpy change involved at the phase transition does provide some indication of the types of phases involved. Accordingly, DSC is used in conjunction with optical polarizing microscopy to determine the type of mesophase that a material exhibits [1-4].

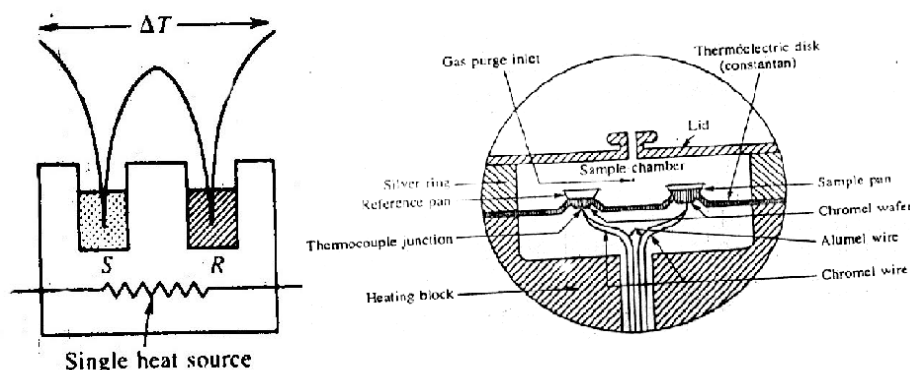


Fig. 1 : Schematic of two furnaces (a) for sample and reference material (b) DSC cell cross section

When a material melts, a change of state occurs from a solid to a liquid and this melting process requires energy (endothermic) from the surroundings. Similarly the crystallization of a liquid is an exothermic process and

energy is released to the surroundings. The DSC instrument measures the energy absorbed or released by a sample as it is heated or cooled. The melting transition from a solid to a liquid is a relatively drastic phase transition in terms of the structural change and this is reflected by the relatively high energy of transition. However, DSC can be similarly used to detect the much more phase transitions that are involved in liquid crystalline materials. Such more subtle structural changes involved in liquid crystal phase transitions are reflected by the relatively small enthalpy changes.

In order to study the phase behavior and associated temperature change, we used the differential scanning calorimeter (Linseis model DSC L63) employs two furnaces, one to heat the sample under investigation and the other to heat an inert reference material. The two furnaces are separately heated but connected by two control loops to ensure that the temperature of both remains identical through a heating or cooling cycle and the heating or cooling rate for each is constantly identical. Experiment was controlled by computer and taking data by instrumental software. Before use, the DSC was calibrated by running a standard material, usually indium and comparing the experimental melting point and enthalpy of transition to the standard values. Each sample was left in the sample pan till we ensured that thermal equilibrium was reached. Then the temperature was allowed to run from room temperature to isotropic of each sample at 5°C/min.

According to the thermal analog of ohm's law

$$Q = \frac{T_2 - T_1}{R_{th}} \quad \dots (1)$$

The heat flow is proportional to the driving force (the temperature difference between temperature T_1 and T_2) and inversely proportional to the thermal resistance, R_{th} combining then preceding relationships yields:

$$\Delta H = Q_s - Q_r = \frac{T_c - T_s}{R_{th}} - \frac{T_c - T_r}{R_{th}} \quad \dots (2)$$

Where T_c is a constant temperature external to the sample and reference, T_s is the sample temperature and T_r is the reference temperature. The system is so designed that the two T_c and two R_{th} values are identical. Thus

equation
$$\Delta H = - \frac{T_s - T_r}{R_{th}} \quad \dots (3)$$

The measurement signal is the voltage from the thermocouple or thermopile, which is proportional to the temperature difference ($T_s - T_r$).

Integration of the area under a DSC curve provides a direct measurement of ΔH for thermally induced transitions according to the equation:

$$A = - K' m \Delta H \quad \dots (4)$$

Where A is the area k' the instrument constant, which is independent of the temperature, m the mass, and H the enthalpy of the reaction or transition. Precise determinations require enlargement of the thermogram for accurate area measurements and a time base display rather than the temperature base thermogram. The data stored on disks are recorded at maximum sensitivity. Thermograms can be re-plotted over a temperature range and on a scale selected by the operator. Temperature expansion to 0.2°C/cm is possible. When this feature is combined with a high calorimetric sensitivity of 0.01mW/cm, thermal occurrences that produce very small amounts of heat can be recorded. For maximum accuracy, a baseline is obtained and subtracted from the sample thermogram to determine the heat capacity. Heats of transitions are calculated from stored data by the applications software of the microcomputer.

IMPORTANCE OF MIXED SYSTEMS:

By mixing two nematogens say X and Y one can obtain a material with a lower melting point while the 'clearing point' T_c is not much depressed. Many of the commercial room-temperature nematics Merk IV the tolans, etc are mixtures of this type, with the composition of the solid-liquid eutectic of minimal melting point.[5-7]

Mixtures of nematogens X with molecules Y of different shapes are also useful. For instance, the internuclear distances of molecules Y can be measured accurately by NMR if the solvent X is nematic. Also, if Y is a chiral molecule, it twists the nematic into a cholesteric: this leads to a new form of polarimetry, where the chiral solute Y is not probed by the optical properties of its own molecule, but rather by the long-range distortions which it creates in X. In many cases it may be of interest to enhance a certain property in a nematic phase X by adding a suitable solute Y.[6-10]

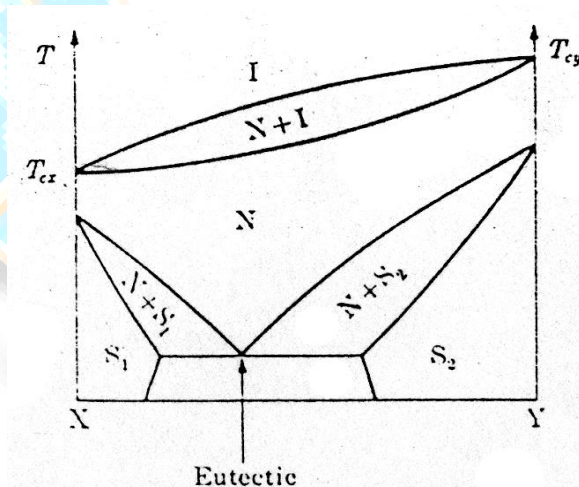


Fig. 2: Typical phase-diagram for a mixture of two nematogens X, Y which are well miscible in the nematic phase N, but not entirely miscible in the solid phase S.

For all these reasons, data on the phase diagrams of mixtures are very important. Some useful examples are given by Gray and a general discussion has been given by Billard. [11]

Theoretical aspect : The classical Clausius-Mossotti equation correlates the dielectric constant (ϵ) of an isotropic medium with its molecular polarizability (α) at low frequencies. Replacing $\epsilon = n^2$, the Lorentz – Lorentz equation correlates the refractive index of an isotropic medium with molecular polarizability in the optical frequencies.

Vuks made a bold assumption that the internal field in a liquid crystal is the same in all directions and gave a semi-empirical equation, correlating the refractive indices with the molecular polarizabilities for anisotropic materials.

$$\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N \alpha_{e,o} \quad \dots(5)$$

In **Equation (5)**, n_e and n_o are refractive indices for the extraordinary and ordinary ray respectively, N is the number of molecules per unit volume, $\alpha_{e,o}$ is the molecular polarizability, and $\langle n^2 \rangle$ is defined as

$$\langle n^2 \rangle = (n_e^2 + 2n_o^2)/3 \quad \dots(6)$$

$$\langle n^2 \rangle^{1/2} = \sqrt{\frac{n_e^2 + 2n_o^2}{3}}$$

or

we call $\langle n^2 \rangle^{1/2}$ as the root mean square (rms) refractive index. Since the sample alignment is planar, the optical anisotropy (Δn) is given by the difference between n_e and n_o i.e.

$$\Delta n = n_e - n_o \quad \dots(7)$$

$$n_e = n_o + \Delta n \quad \dots(8)$$

Putting the value of n_e from **Equation (8)** in **Equation (6)** and solving it we get a quadratic equation in (n_o), given as,

$$\langle n^2 \rangle = \left\{ \frac{(n_o + \Delta n)^2 + 2n_o^2}{3} \right\}$$

$$\langle n^2 \rangle = \left[\frac{n_o^2 + (\Delta n)^2 + 2n_o\Delta n + 2n_o^2}{3} \right]$$

or

$$3n_o^2 + 2(\Delta n)n_o + (\Delta n)^2 - 3\langle n^2 \rangle = 0 \quad \dots(9)$$

Solving **Equation (9)** for n_o , we get,

$$n_o = \langle n^2 \rangle^{1/2} - \left(\frac{1}{3} \right) (\Delta n) \quad \dots(10)$$

Using **Equations (7) & (10)**,

$$n_e = \langle n^2 \rangle^{1/2} + \left(\frac{2}{3} \right) (\Delta n) \quad \dots(11)$$

We have described n_e & n_o as a function of $\langle n \rangle$ and Δn in the form:

$$n_o = \langle n \rangle - \left(\frac{1}{3} \right) (\Delta n) \quad \dots(12)$$

$$n_e = \langle n \rangle + \left(\frac{2}{3} \right) (\Delta n) \quad \dots(13)$$

$$\langle n \rangle = \left(\frac{n_e + 2n_o}{3} \right) \quad \dots(14)$$

where

We can find data for n_e & n_o & we have calculated the values of $\langle n \rangle$, $\langle n^2 \rangle$ and $\langle n^2 \rangle^{1/2}$ [13, 15].

Order parameter in nematic liquid crystal mixture:

The order in the liquid crystal is affected by various microscopic properties, e.g., dielectric constant, magnetic susceptibility, refractive index, viscosity etc.

Optical isotropy is observed, if light passes parallel to the director, where as optical birefringence is observed if the light passes in the direction perpendicular to the director. Polarized rays parallel to the director have a different index of refraction from those polarized perpendicular to the director. Many experiments demonstrate that the anisotropy of nematics arise because of the tendency of the rod like molecules in the fluid to align their

long axis parallel to the director. This is shown schematically in **Fig.3(a)** The director is denoted by the symbol $\hat{n}$; the rod-like molecules are represented by the short lines[12].

In **Fig.3(b)**, let the director lie along the z-axis of a fixed rectangular co-ordinate system. The orientations of the rod-like molecule can then be described using the three Eulerian angles shown. If any angle Ψ or ϕ was in some way preferred, a symmetry lower than cylindrical would necessarily result. Thus, we are left with the remaining angle θ as the only one for which any degree of order can exist. If any angle θ is preferred, then resultant symmetry is indeed cylindrical, the most probable or the preferred, angle in nematics has been shown experimentally to be $\theta = 0$, the long molecular axis parallel to $\hat{n}$. If there is no preference to a particular θ , then all such angles become equally probable and complete isotropy results ; this is the isotropic normal liquid phase.

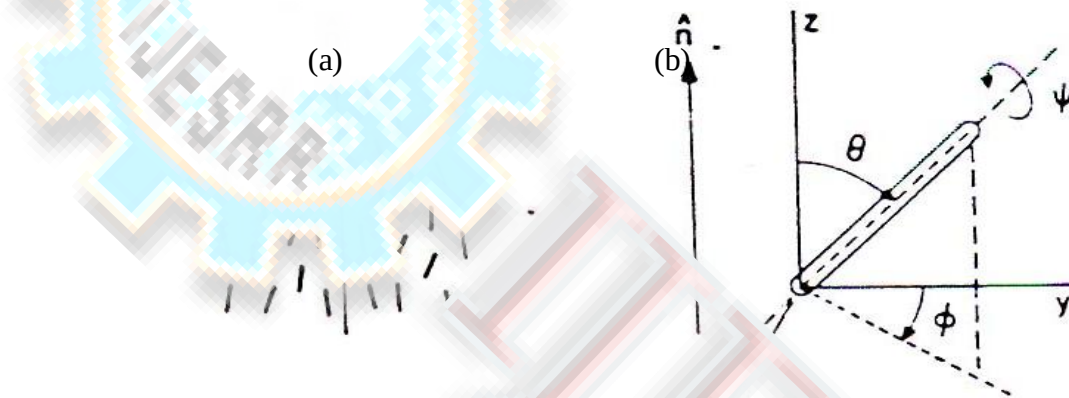


Fig.3: Schematic representation of the structure of (a) nematic liquid crystal (b) The Euler angles required to describe the orientation of a molecule in nematic liquid crystal.

When all the molecules are fully aligned with $\hat{n}$, all $\theta = 0$ and $\langle \cos^2 \theta \rangle = 1$. On the other hand, if the molecules are randomly distributed in direction, all values of θ are equally likely and $\langle \cos^2 \theta \rangle = 1/3$. By tradition, the order parameter in any order-disorder problem is always taken such that it is unity in the perfectly ordered phase and vanishes for the completely disordered phase. Examination of the average values described above shows that the proper order parameter for the nematic liquid crystal is

$$\langle P_2 \rangle = \frac{1}{2} (3 \langle \cos^2 \theta \rangle - 1) \quad \dots(15)$$

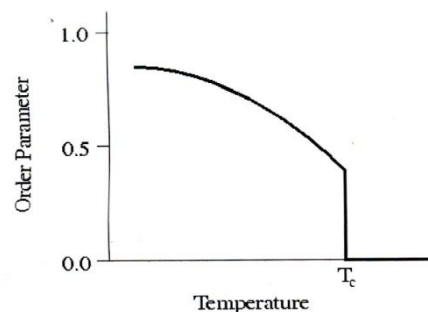


Fig. 4: Typical order parameter vs. temperature in a nematic liquid crystal material.

Clearly, $\langle P_2 \rangle = 1$ for the completely ordered nematic phase and $\langle P_2 \rangle = 0$ for the disorder isotropic phase. The symbol $\langle P_2 \rangle$ is used for the order parameter because we recognize the particular combination in above equation to be the second-order Legendra polynomial, $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$. In the original theory as well as in much of the literature, the symbol S is used to represent $\langle P_2 \rangle$. Values of $\langle P_2 \rangle$ between 0 and 1 describe degrees of ordering intermediate between completely isotropic and completely ordered. It is the task of order-disorder the to determine the temperature dependence of $\langle P_2 \rangle$ and shown in **Fig-4**, In typical nematic phases, $\langle P_2 \rangle$ lies in the region of 0.4 to 0.8 indicating that the molecules are rather disorder.

CONCLUSIONS:

In theory clearly indicated the indexes (n_e , n_o) and birefringence (Δn) order parameter as a function of temperature. A linear relation was given in between birefringence (Δn) and order-parameter. The normalized polarizabilities and order parameter have been determined at different temperatures. Temperature effect clearly seen in optical properties study.

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