CHAPTER 2
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Orientational order parameter from density and refractive index measurements

2.1 Introduction

The liquid crystal (LC) display technology is the major area which requires enormous data on the liquid crystalline materials, their response to electrical fields and the study regarding optical anisotropies. Hence, it is very important to gain the knowledge of the temperature dependence of the densities, refractive indices, molecular polarizabilities and the order parameter of the liquid crystalline materials.

The main property of a LC that distinguishes it from an isotropic liquid is its long-range orientational order defined by the order parameter, $S$. This property is inherent in all mesophases. The orientational order parameter is the most important quantity and it enters into many expressions regarding extensive physical properties [1-4]. The orientational order parameter is strongly temperature dependent because increase in temperature disturbs the order owing to thermal agitation. The orientational order parameter $S$ in the liquid crystalline phase can be estimated using its intrinsic properties or techniques such as optical, dielectric, diamagnetic susceptibility, elastic constants, X-rays, NMR, etc [3,4]. These physical properties can also be effectively employed to study the temperature dependence of $S$. However, optical method is most widely used for this purpose. Optical method usually involves measurement of refractive indices and density as a function of temperature, accompanied by the calculation of polarizabilities [5-7].

The study of temperature variation of density ($\rho$), a bulk property, across different phases in LC materials provides information regarding the nature of the phase transition (whether first or second order) and the growth of the pre-transitional effects [8-11]. Further, such studies provide complimentary and confirmatory experimental evidence for the results obtained using other techniques, such as polarizing thermal microscopy and differential scanning calorimetry (DSC) regarding the determination of phase transition temperatures and the thermal stability of the phase of interest.

Birefringence of LCs plays a major role in the technical applications of liquid crystals. Optimization of optical properties of liquid crystal display devices requires the knowledge of refractometric data of LCs. The nematic phase exhibits high,
positive birefringence which is strongly dependent on temperature and frequency [12-14].

Since the discovery of importance of LCs in technical applications, numerous attempts were made by researchers all over the world to synthesize new liquid crystalline materials. Among such materials, the $N$-(p-$n$-alkoxybenzylidene)-p-$n$-alkylanilines, popularly known as the Schiff’s base $nO.m$ compounds (where $n$ and $m$ denote the alkyl chain lengths on either side of the rigid core) were the first single component room temperature LCs to be synthesized. This homologous series exhibits subtle but complex polymorphism. By changing the position of oxygen atom on either side of the benzylidene core, $nO.m$, $n.Om$, $nO.Om$ and $n.m$ series of compounds are obtained. The electro-negative oxygen atom plays an important role in deciding the clearing temperature as well as the phase variants. It is well established that the oxygen atom in the molecular moiety enhances the clearing temperatures as well as the nematic phase abundance in a homologous series. The easy and relatively inexpensive synthesis procedure of these compounds has prompted several investigators to use them for the study of fundamental aspects of LCs [15].

Literature survey reveals that a number of workers in the field of liquid crystals have synthesized the Schiff base compounds and have studied their physical properties using various techniques such as calorimetric, optical, X-rays, NMR, ESR, etc. [16-29]. There have been a number of reports on computation of orientational order parameter $S$ in these compounds using density and refractive index measurements [19,20,25-29].

$N$-(p-$n$-methoxybenzylidene)-p-$n$-butylaniline (MBBA/1O.4), the first synthetic room temperature LC has been extensively studied by different techniques [16-18].

Revannasiddaiah and Krishnamurti [19] have estimated the order parameter of p-propoxybenzylidene p-pentylaniline (3O.5) and p-butoxybenzylidene p-pentylaniline (4O.5) from birefringence and density measurements and using bond polarizability data. Densities were measured using capillary tube technique and refractive indices were measured using small angle hollow prism technique. Polarizabilities and internal field constants were estimated using Neugebauer model. Nagappa et al. [20] have carried out similar studies on 2O.4 (EBBA), 3O.5 (PBPA), 4O.5 (BBPA) and binary mixtures of 3O.5 and 2O.4, and 4O.5 and 3O.5. The order
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The orientational order parameter has been computed using the law of additivity of binary mixtures and these values are found to agree with the experimentally determined values.

Pisipati and his group have carried out extensive studies on several nO.m compounds using thermal microscopy, DSC, density, ultrasonic velocity, magnetic resonance and X-ray diffraction techniques [21-29]. They have reported refractive index and density measurements of 4O.m compounds with \( m = 4 \) to 10, 12 to 16 [21]. Rao et al. [29] have carried out refractive index and density measurements of 1O.12, 1O.14, 2O.12 and 2O.14 compounds. The effective polarizabilities \( \alpha_e \) and \( \alpha_o \) were calculated using Vuks and Neugebauer local field models. The order parameter \( S \) has been estimated using different methods. The results obtained are compared and discussed.

Sailaja [30] has studied the fluctuation spectra of 4O.2, 4O.3 and 4O.4 compounds using field cycling NMR technique. Trivikaram [31] has studied the dynamic molecular processes of 4O.2, 4O.3, 4O.4 and mixture of 4O.2 and 4O.4 through frequency dispersion measurements using field cycling NMR process.

In this chapter, the author has reported the refractive index and density data of:

(i) \( p \)-butoxybenzylidene \( p \)-ethylaniline (4O.2)
(ii) \( p \)-butoxybenzylidene \( p \)-propylaniline (4O.3)
(iii) \( p \)-methoxybenzylidene \( p \)-decylaniline (1O.10)

at different temperatures in their nematic and isotropic phases. The polarizabilities, Lorentz field factors and orientational order parameter of these three compounds are also discussed. Figure 2.1 shows the general structure of nO.m compounds.

\[
\text{Figure 2.1: General structure of nO.m compounds}
\]

2.2 Theory

As is well known, the order parameter, \( S \) is given by the relation,

\[
S = \frac{\alpha_e - \alpha_o}{\alpha_m - \alpha_\perp}
\]

(2.1)

where \( \alpha_e \) and \( \alpha_o \) are respectively the average effective polarizabilities for the extraordinary and ordinary ray, and \( \alpha_m \) and \( \alpha_\perp \) are the polarizabilities of the
molecule when the electric vector is respectively parallel and perpendicular to the long axis of the molecule. The calculation of $\alpha_e$ and $\alpha_o$ involves assumptions with regard to the nature of the local field in the medium and two methods, viz., (i) the use of Vuks formulae [32] and (ii) the use of Neugebauer relations [33] have been commonly adopted by earlier workers [5-7,19,20,25-29]. When no refractive index and density data are available for the crystalline phase, methods such as Haller extrapolation method [34], Lippincott $\delta$-function method [35], bond polarizability method [19,20], molecular vibration method [36], etc. can be used to estimate the value of polarizability anisotropy ($\alpha_{||}-\alpha_{\perp}$). From these values, $S$ can be estimated using equation 2.1.

In the present work, for the reasons cited in the literature [37], the author has used the Neugebauer model to evaluate $\alpha_e$ and $\alpha_o$. The Haller extrapolation method has been used to estimate ($\alpha_{||}-\alpha_{\perp}$). These values have been used to estimate the orientational order parameter $S$ for all the three compounds. The details of these methods are briefly discussed in sections 2.2.1 and 2.2.2.

2.2.1 Effective polarizabilities ($\alpha_e$ and $\alpha_o$) using Neugebauer model

From the measured refractive index and density data in the nematic and isotropic phases, it is possible to calculate the values of the effective polarizabilities $\alpha_e$ and $\alpha_o$ and the mean polarizability $\bar{\alpha}$ using the following Neugebauer relation and Lorenz-Lorentz relation.

The Neugebauer relation [33] for the nematic medium is given by

$$\frac{1}{\alpha_e} + \frac{1}{\alpha_o} = \frac{4\pi N_{lc}}{3} \left[ \left( \frac{n_e^2 + 2}{n_e^2 - 1} \right) + \left( \frac{2(n_o^2 + 2)}{n_o^2 - 1} \right) \right]$$

(2.2)

where $N_{lc}$ is the number of molecules per unit volume in the liquid crystalline phase.

The Lorenz-Lorentz relation for an isotropic medium is given by

$$\bar{\alpha} = \frac{3}{4\pi N_l} \left( \frac{n_l^2 - 1}{n_l^2 + 2} \right) = \frac{(\alpha_e + 2\alpha_o)}{3} = \frac{(\alpha_{||} + 2\alpha_{\perp})}{3}$$

(2.3)

where $N_l$ and $n_l$ correspond to the number of molecules per unit volume and the refractive index respectively in the isotropic (liquid) phase.

To calculate $\alpha_e$ and $\alpha_o$ from Neugebauer method, it is necessary to solve the simple quadratic equation involving ($\alpha_e/\alpha_o$), the quadratic equation being obtainable
from Eqs. 2.2 and 2.3. The molecules discussed here have an elongated shape. The nematic phase is uniaxial positive, and evidently here $\alpha_e > \alpha_o$. Hence, the solution which gives $\alpha_e > \alpha_o$ is chosen.

The expressions relating the refractive indices ($n_e$ and $n_o$), effective polarizabilities ($\alpha_e$ and $\alpha_o$) and the corresponding Lorentz field factors ($L_e$ and $L_o$) are of the form [33]:

$$n_e^2 - 1 = 4\pi N k \alpha_e (1 - 4\pi N k L_e \alpha_e)^{-1} \quad (2.4)$$
$$n_o^2 - 1 = 4\pi N k \alpha_o (1 - 4\pi N k L_o \alpha_o)^{-1} \quad (2.5)$$

The Lorentz field factors can be estimated using Eqs. 2.4 and 2.5. Further, the Lorentz field factors satisfy the relation $L_e + 2L_o = 1$.

### 2.2.2 Polarizability anisotropy ($\alpha_{||} - \alpha_{\perp}$) using Haller extrapolation method

As represented in Figure 2.2, Haller extrapolation method [34] involves the graphical plot of $\log(\alpha_e - \alpha_o)$ against $\log[1 - (T/T_{NI})]$, where $T_{NI}$ is the nematic-isotropic transition temperature. The straight line graph obtained is extrapolated to $T=0K$. The value of $(\alpha_{||} - \alpha_{\perp})$ can be obtained from the corresponding y-intercept.

![Figure 2.2: Plot of log(\alpha_e - \alpha_o) versus log[1 - (T/T_{NI})]](image)
2.3 Experimental

2.3.1 Determination of transition temperatures

The compounds 4O.2, 4O.3 and 1O.10 used in the present work were procured from M/s Frinton Laboratories Inc., USA (purity 99%). The phase sequence and transition temperatures of the compounds were studied using polarizing microscope and DSC. Compound 1O.10 is purely nematic whereas the compounds 4O.2 and 4O.3 exhibit both nematic and SmG phases. Table 2.1 gives the phase sequence exhibited by the compounds along with the transition temperatures. Figure 2.3 shows the polarizing microscope (model SDTECHS-SD-VPM2727) in conjunction with a hot stage used to study the transition temperatures and to record the optical textures exhibited by the samples. The texture photographs of the compounds recorded using the polarizing microscope are given in Figures 2.4-2.8.

**Table 2.1: Phase sequence and transition temperatures of 4O.2, 4O.3 and 1O.10**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase sequence and transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4O.2</td>
<td>(Cr) 31.07 (SmG) 50.66 (N) 65.65 (I)</td>
</tr>
<tr>
<td>4O.3</td>
<td>(Cr) 28.64 (SmG) 49.96 (N) 79.22 (I)</td>
</tr>
<tr>
<td>1O.10</td>
<td>(Cr) 40.51 (N) 59.90 (I)</td>
</tr>
</tbody>
</table>
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Figure 2.3: Polarizing microscope with hot stage and other accessories

Figure 2.4: Schlieren texture of nematic phase in 4O.2 recorded at 62.4°C (40x)
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Figure 2.5: Mosaic texture of smectic G phase in 4O.2 recorded at 43.2°C (40x)

Figure 2.6: Droplet texture of nematic phase in 4O.3 recorded at 78.8°C (40x)
Figure 2.7: Mosaic texture of smectic G phase in 4O.3 recorded at 43.5°C (40x)

Figure 2.8: Droplet texture of nematic phase in 1O.10 recorded at 59.5°C (40x)
2.3.2 Measurement of density

The density ($\rho = m/V$) of a substance is defined as the mass per volume and is generally determined by measuring the volume ($V$) of a known mass ($m$) of a substance. The density measurement (dilatometry) is useful in determining the order of phase transition, pre-transition behavior and critical exponent. Parameters such as specific volume ($v = 1/\rho$), molar volume ($M_v = \text{molecular weight/ density}$), the thermal expansion coefficient [$\alpha = (1/M_v) (dM_v/dT)$] of the material, etc. can also be obtained from the dilatometric studies. Fundamentally, the density is related to the derivatives of Gibbs free energy ($G$). The first order transition is characterized by a discontinuity or a steep change in specific volume associated with a thermal expansion coefficient.

For the determination of density of the liquid crystalline materials at different temperatures, a hot oven with a provision for the observation of levels of liquid crystal material in the capillaries is essential. For this purpose, a specially constructed pyknometer and a hot oven (i.e., density block) were used. The details of their construction are discussed below.

2.3.2.1 Construction of hot oven (or density block)

The density block (Figure 2.9) consists of three brass blocks of 1.5 cm thick, 40 cm length and 10 cm width arranged in rectangular shape with the fourth side opening for the arrangement of glass panel for observation. Each brass block is connected to an electrical heater of 250 watt at 220 volt A.C. having dimensions 40 cm x 6 cm x 3 mm. To maintain uniform temperature throughout the volume of oven, air circulation is maintained by fixing a fan at the bottom of the oven. The whole assembly is covered with thermal insulating sheets to prevent thermal shocks. The glass doors are fixed to the front side of the density block in order to make provision to observe the LC levels in the capillaries. The temperature of the block was varied by controlling a continuously variable auto transformer. The temperature inside the block was measured with an accuracy of ±0.1°C using a thermocouple.

2.3.2.2 Density measurements using pyknometer

The pyknometer consists of capillaries with a diameter of about 300 microns and 15 to 20 cm length arranged at the top of U-shaped glass tube having bore of diameter about 6-8 mm (Figure 2.10). The bottom of the pyknometer contains about
96% of total volume of the sample. The absolute capacity of the pyknometer is about 0.87 cc. The accuracy of the density measurement is ± 0.0001 g/cm³.

The pyknometer was calibrated by measuring the molar volume of water at different levels. The mass of the sample was measured using a chemical balance with an accuracy of ±0.0001 gm. For filling the pyknometer with the sample, the pyknometer was placed in the heating chamber (hot oven or density block) as shown in Figure 2.11. The temperature of the density block was raised to 10°C above the clearing point ($T_{NI}$) of the LC sample by controlling the auto transformer. The sample was slowly filled inside the pyknometer until the sample level reaches the mark on the capillaries. Air bubbles formed were carefully eliminated by blowing air into the capillary using a rubber hose. The density block was slowly cooled to a temperature approximately 5°C above $T_{NI}$. The excess sample in the cups of the capillaries was removed using a syringe.

The sample level in the capillaries was observed using a modified cathetometer (Figure 2.12) in the cooling cycle. It has a telescope with about 6 to 8x magnification. The main scale of the cathetometer is graduated in mm and each division corresponds to 0.5 mm. The vernier with 50 divisions is attached to the main scale corresponding to the least count of 0.01 mm. Observation of a number of readings using conventional cathetometer is tedious. Hence, the cathetometer was modified to conduct the experiment with ease and accuracy. The main scale and the vernier were replaced with a digital scale which gives an accuracy of ±0.01 mm. Instead of viewing through the telescope eyepiece, a CCD camera was attached to the telescope and the sample levels in the capillaries were observed on a 14” T.V with very high magnification.

The densities of the samples were measured at different temperatures in the nematic and isotropic phases in steps of 0.1°C as described above. The measured densities and thermal expansion coefficients of all the three compounds are shown graphically in Figures 2.13-2.15.
Figure 2.9: Schematic diagram of the density block

Figure 2.10: Schematic diagram of the pyknometer
Figure 2.11: Density block with pyknometer

Figure 2.12: Modified cathetometer
Figure 2.13: Variation of density ($\rho$) and thermal expansion coefficient ($\alpha$) with temperature in 4O.2

Figure 2.14: Variation of density ($\rho$) and thermal expansion coefficient ($\alpha$) with temperature in 4O.3
2.3.3 Measurement of refractive indices

In the present work, refractive indices of the samples 4O.2, 4O.3 and 1O.10 have been measured using the small angle hollow prism technique developed by Chatelain [38] using a modified spectrometer. The temperature of the LC samples was controlled to an accuracy of ±0.1°C using a specially constructed hot chamber. The details of the fabrication of small angle hollow prisms and the construction of hot chamber and modified spectrometer are given below.

2.3.3.1 Fabrication of small angle hollow prisms

Small angle hollow prisms (of prism angle about 30-40°) were prepared using two optical flats (thickness ≈ 3 mm, length 5 cm and breadth 2.5 cm) with a thin glass plate as spacer, and glue as shown in Figure 2.16. The angle of the prism was measured accurately using a modified spectrometer. In order to get two sharp refracted beams, the sample has to be well aligned. For this purpose, the inner faces of the optical flats were rubbed in a direction parallel to the refracting edge of the prism (which is the desired direction of orientation). The sample was filled by allowing a small quantity of the LC sample in the isotropic phase to flow slowly into the prism at its refracting edge by capillary action. The combination of rubbing and flowing ensures the homogeneous alignment of the nematic sample with the optic axis.
parallel to the rubbing direction. The edge of the prism was sealed by gluing a thin glass plate so as to prevent the LC sample from flowing outside the cell.

![Figure 2.16: Schematic diagram of the small angle hollow prism](image)

2.3.3.2 Construction of hot chamber

The birefringence of nematic LCs is strongly temperature dependent. The temperature change of even 0.1°C can alter the birefringence of the sample significantly, especially near the nematic-isotropic transition temperature. Hence, the temperature of the sample has to be controlled precisely with an accuracy of at least ±0.1°C. For this purpose, a specially constructed hot chamber made of brass block was used (Figure 2.17). The entire assembly was covered by thick thermal insulating sheets on all the sides to minimize heat radiation. The prism was placed inside the hot chamber by removing the top plate of the chamber. Small windows are placed on either sides of the block to allow the propagation of incident and refracted light beam.

![Figure 2.17: Cross sectional view (top view) of the hot chamber used for refractive index measurements](image)

The block was heated by applying voltage to the heating element and controlling the temperature continuously with variable auto transformer. Temperature of the experimental samples could be varied from 30°C to 200°C by applying voltages of the order of 20V to 100V. A thermocouple was placed inside the hot chamber, close to the sample and temperature was read using a digital thermometer.
2.3.3.3 Refractive index measurements using a modified spectrometer

Refractive indices of LCs can be measured using critical angle refractometers such as Abbe or Pulfrich refractometers by choosing a proper glass prism possessing the refractive index higher than that of liquid crystal. However, these ordinary laboratory spectrometers suffer from the disadvantage of low resolution of the telescope and inaccuracy of the vernier to give absolute or relative values of the refractive index of the LC material under study. Hence, for accurate measurement of refractive indices, ordinary laboratory spectrometer was modified by installing some discrete parts such as an objective with long focal length, an ocular scale etc., so as to improve its resolution and accuracy. Although constructing the telescope part of a spectrometer from discrete parts inevitably sacrifices some of its features, the working of the modified spectrometer (Figure 2.18) is quite satisfactory and comparable to other methods as far as quantitative observations of liquid crystalline samples are concerned. Moreover, the modified laboratory spectrometer is of low cost with easy operation and can be used to measure the refractive index of highly viscous liquids with no upper limiting value of refractive index. The refractive indices measured with a goniometer spectrometer usually has an accuracy of 2° of an arc i.e. ±0.001° [7] while the accuracy of the modified spectrometer is ±0.0004°.

The schematic diagram of the modified spectrometer is shown in Figure 2.19 and its construction details are shown in Figure 2.20. It consists of a long focal length objective (f = 40 cm, aperture = 4.5 cm). A reflecting prism is arranged on the optic axis for convenience to observe the images in the horizontal plane instead of vertical plane. The measuring unit for lateral movements of the transmitted beams consists of (Figure 2.21):

i. A cross called an index line mount (thickness = 10 μm) to adjust the zero-zero coincidence of index line and drum head reading [Figure 2.21 (a)],

ii. A scale mount carrying calibrated ocular scale of 50 divisions each corresponding to one minute, which can be moved laterally (i.e., horizontal plane of the prism table) over the fixed index line by using drum head and

iii. A drum head with 40 divisions which is attached to the ocular scale.

The 40 divisions on the drum head correspond to one minute (1 div) in the ocular scale, i.e., each division of drum head are equal to 1.5 seconds of arc. The ocular scale is fixed in a brass block which is machined as a down tail. The scale can be
viewed through the eye piece (20x). In order to check the accuracy of the spectrometer, refractive indices of 20.4/ EBBA were measured. The results obtained were found to be in good agreement with the reported data [39]. For cells with wedge angle = 1°, the birefringence (\( \delta n \)) upto 0.8 can be measured in the field of view of the ocular scale without the rotation of the telescope.

For the measurement of refractive index in the nematic phase, the sample was filled inside the small angle hollow prism as described in section 2.3.3.1. The prism was placed inside the hot chamber and the temperature of the chamber was increased to about 10°C above \( T_{NI} \). Refractive index measurements were started at 5°C above \( T_{NI} \). In the isotropic phase, only one refracted image is seen in the field of view of the telescope. When the sample goes into the nematic phase, two refracted images are seen, corresponding to ordinary and extraordinary rays. The angle of deviation is larger for extraordinary ray than that for ordinary ray. All the readings were taken by setting the prism in the minimum deviation position. The well-known relation for determining the refractive indices \( n_i \) (\( i = o, e \) corresponding to the ordinary ray and extraordinary ray) in the case of small angle hollow prism is:

\[
 n_i = \frac{\sin \left( \frac{(A + D_i)/2}{\sin (A/2)} \right)}{\sin (A/2)} \quad (2.9)
\]

where \( A \) is the angle of the small angle hollow prism and \( D_i \) (\( i = o, e \)) is the angle of deviation. In this case, both \( A \) and \( D \) are less than 1°. Hence, using the relation \( \sin \theta \approx \theta \) for small values of \( \theta \), Eq. 2.9 reduces to:

\[
 n_i = 1 + \frac{D_i}{A} \quad (2.10)
\]

where \( D \) is given by:

\[
 D = \text{deviation} = \text{Ocular scale reading} + \left( \frac{1}{60} \times \frac{3}{2} \times \text{Drumhead reading} \right)
\]

The measurement of refractive indices in the nematic and isotropic phases were carried out for all the three samples at various temperatures for \( \lambda = 5893\AA \). The measured refractive indices are shown graphically in Figures 2.22-2.24. Refractive indices for some selected temperatures are also shown in Table 2.2. The variation of the birefringence \( \delta n \) with \( T_{NI}-T \) in the nematic phase of all the compounds is shown in Figure 2.25.
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Figure 2.18: Modified spectrometer and its accessories

Figure 2.19: Schematic diagram of the modified spectrometer
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Figure 2.20: Construction details of the modified spectrometer

Figure 2.21: Callibrated ocular scale of the modified spectrometer (a) Adjustment of zero-zero coincidence (b) Taking a reading
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Figure 2.22: Variation of refractive indices $n_e$ and $n_o$ with temperature in 4O.2

Figure 2.23: Variation of refractive indices $n_e$ and $n_o$ with temperature in 4O.3
Figure 2.24: Variation of refractive indices $n_e$ and $n_o$ with temperature in 1O.10

Figure 2.25: Variation of birefringence ($\delta n$) with $(T_{NI}-T)$ in 4O.2, 4O.3 and 1O.10
Table 2.2: Refractive indices in the nematic and isotropic phases of 4O.2, 4O.3 and 1O.10 for \( \lambda = 5893 \AA \)

<table>
<thead>
<tr>
<th></th>
<th>4O.2</th>
<th>4O.3</th>
<th>1O.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (°C)</td>
<td>n_e</td>
<td>n_o</td>
<td>t (°C)</td>
</tr>
<tr>
<td>70.5</td>
<td>1.5794</td>
<td>1.5794</td>
<td>84</td>
</tr>
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<td>69.5</td>
<td>1.5804</td>
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2.4 Results and discussion

From the experimental density data (Figures 2.13-2.15), the density jump, \((\Delta \rho / \rho)\) was calculated as the vertical distance between the density values \((\rho_1 \text{ and } \rho_2)\) obtained by the linear extrapolation from either sides of the transitions, (which are in fact the average value of the above two extrapolated density values i.e., \([((\rho_1 - \rho_2))/((\rho_1 + \rho_2)/2)]\)). The values of the thermal expansion coefficient maxima \((\alpha_{\text{max}})\) at \(T_{NI}\), slope of the density variation with temperature \((d\rho/dT)\) across the nematic and isotropic phases in the equilibrium state, the observed percentage density jump \((\Delta \rho / \rho)\) at \(T_{NI}\) and the molar volume \((M_V)\) at \(T_{NI}+5\text{K}\) for all the compounds are given in Table 2.3. The variation of molar volume with alkyl chain length \((n+m)\) is shown in Figure 2.26.
The salient features observed from the dilatometric studies are:

1. From Figures 2.13-2.15 it is observed that density decreases monotonically with the increase of temperature in the nematic phase and in the vicinity of \(T_{NI}\) it shows a steep decrease, before it attains equilibrium value of the isotropic phase.

2. The isotropic-nematic (I-N) transition temperatures observed in the density measurements are in agreement with those observed from polarizing microscope, DSC and birefringence measurements.

3. The values shown in the Table 2.3 agree well with those reported in literature for other nO.m compounds [22-27].

4. The distinct density jumps and the thermal expansion coefficient maxima suggest that the I-N transition nature is of first order.

5. The higher values of slopes of density variation with temperature in equilibrium nematic phase in these compounds than in the isotropic region indicate an additional molecular packing in the nematic phase with orientational order and the accompanying growth of long range orientational order from a completely disordered molecular arrangement in the isotropic phase.

6. The average variation of molar volume per methylene is found to be 15.93x10^{-6} \, m^3\cdot mol^{-1} which agrees well with the literature data available on nO.m compounds in which this value varies between 15 and 17x10^{-6} \, m^3\cdot mol^{-1} [22-27].

### Table 2.3: Thermal expansion coefficient maxima, slopes of density in isotropic (I) and nematic (N) phases, density jump and molar volume in 4O.2, 4O.3 and 1O.10

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\alpha_{\text{max}}) (I-N) ((10^{-4}/^\circ\text{C}))</th>
<th>((d\rho/dT)) ((10^{-4} , \text{g}\cdot\text{cm}^{-3}/^\circ\text{C}))</th>
<th>(%) of ((\Delta\rho/\rho)) I-N</th>
<th>(M_V(\text{NI+5K})) ((10^{-6} , \text{m}^3\cdot\text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4O.2</td>
<td>50.54</td>
<td>3.30</td>
<td>8.17</td>
<td>0.28</td>
</tr>
<tr>
<td>4O.3</td>
<td>50.10</td>
<td>3.77</td>
<td>8.64</td>
<td>0.27</td>
</tr>
<tr>
<td>1O.10</td>
<td>71.50</td>
<td>4.18</td>
<td>9.17</td>
<td>0.45</td>
</tr>
</tbody>
</table>
From the measured refractive index data (Figures 2.22-2.24) it is observed that:

1. The refractive index in the isotropic phase shows very nominal increment with the decrease of temperature.

2. At the I-N phase transformation, the isotropic ray splits into two rays which indicates the onset of birefringence, one value higher and another lower than isotropic value corresponding to extraordinary ($n_e$) and ordinary refractive ($n_o$) indices respectively. This is clearly observed in the telescope of the modified spectrometer at the angle of minimum deviation.

3. In the nematic region, the $n_e$ increases while the $n_o$ decreases with the decrease of temperature.

4. The I-N transition temperatures observed in the birefringence measurements are in agreement with those observed from polarizing microscope, DSC and density measurements.
From the measured refractive index and density data, effective polarizabilities $\alpha_e$ and $\alpha_o$, Lorentz field factors $L_e$ and $L_o$ and orientational order parameters $S$ have been estimated using Neugebauer model (Eqs. 2.2-2.5). The values obtained (at selected temperatures) are given in Tables 2.4-2.6.

The values of $(\alpha_\parallel - \alpha_\perp)$ estimated for the compounds 4O.2, 4O.3 and 1O.10 using Haller extrapolation method are found to be $24.09 \times 10^{-24}$ cm$^3$, $25.29 \times 10^{-24}$ cm$^3$ and $32 \times 10^{-24}$ cm$^3$ respectively.

The order parameters for all the three compounds have been determined using the estimated values of $\alpha_e$, $\alpha_o$ and $(\alpha_\parallel - \alpha_\perp)$. The observed values of $S$ are shown graphically in Figure 2.27. From the figure, it may be noted that the trend of variation of the $S$ factors in all the compounds agree well with those reported in literature for other nO.m compounds [19,20,25-29].

As may be seen from Tables 2.4-2.6 and Figure 2.28, the value of $L_e$ increases while the anisotropy in Lorentz field factors ($L_o - L_e$) decreases with increasing temperature. The anisotropy of the molecular distribution is zero at $T_{NI}$. The decrease in the anisotropy of Lorentz field factors is consistent with the expectation that the molecular distribution should be less anisotropic with increase of temperature. In fact, a graphical representation of the values of ($L_o - L_e$) with the corresponding values of $S$ factors strikingly shows that the anisotropy of molecular distribution decreases progressively with the decreasing order parameter, the variations being approximately linear (Figures 2.29-2.31).

In the next chapter, we have discussed the translational order parameter in the SmB phases of (i) 4-hexyl-4’-[2-(4-isothiocyanatophenyl)ethyl]-1-1’-biphenyl (HIEB) and (ii) p-butoxybenzylidene p-heptylaniline (4O.7).
### Table 2.4: Effective polarizabilities, Lorentz field factors and orientational order parameter of 4O.2

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>$\alpha_e$</th>
<th>$\alpha_o$</th>
<th>$(\alpha_e - \alpha_o)$</th>
<th>$L_e$</th>
<th>$L_o$</th>
<th>$(L_o - L_e)$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>43.614</td>
<td>35.718</td>
<td>7.897</td>
<td>0.297</td>
<td>0.358</td>
<td>0.061</td>
<td>0.328</td>
</tr>
<tr>
<td>64</td>
<td>44.167</td>
<td>35.412</td>
<td>8.755</td>
<td>0.290</td>
<td>0.361</td>
<td>0.070</td>
<td>0.363</td>
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<tr>
<td>63</td>
<td>44.600</td>
<td>35.211</td>
<td>9.389</td>
<td>0.284</td>
<td>0.361</td>
<td>0.077</td>
<td>0.390</td>
</tr>
<tr>
<td>62</td>
<td>44.960</td>
<td>35.056</td>
<td>9.904</td>
<td>0.280</td>
<td>0.362</td>
<td>0.082</td>
<td>0.411</td>
</tr>
<tr>
<td>61</td>
<td>45.275</td>
<td>34.866</td>
<td>10.409</td>
<td>0.277</td>
<td>0.364</td>
<td>0.087</td>
<td>0.432</td>
</tr>
<tr>
<td>60</td>
<td>45.644</td>
<td>34.669</td>
<td>10.976</td>
<td>0.274</td>
<td>0.367</td>
<td>0.093</td>
<td>0.456</td>
</tr>
<tr>
<td>59</td>
<td>46.066</td>
<td>34.532</td>
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<td>0.270</td>
<td>0.368</td>
<td>0.098</td>
<td>0.476</td>
</tr>
<tr>
<td>58</td>
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<td>34.388</td>
<td>11.945</td>
<td>0.267</td>
<td>0.369</td>
<td>0.102</td>
<td>0.496</td>
</tr>
<tr>
<td>57</td>
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<td>34.244</td>
<td>12.378</td>
<td>0.265</td>
<td>0.370</td>
<td>0.106</td>
<td>0.514</td>
</tr>
<tr>
<td>56</td>
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<td>34.103</td>
<td>12.801</td>
<td>0.262</td>
<td>0.372</td>
<td>0.110</td>
<td>0.531</td>
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<tr>
<td>55</td>
<td>47.169</td>
<td>33.970</td>
<td>13.199</td>
<td>0.259</td>
<td>0.373</td>
<td>0.114</td>
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</tr>
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<td>54</td>
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<td>0.256</td>
<td>0.374</td>
<td>0.118</td>
<td>0.564</td>
</tr>
<tr>
<td>53</td>
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<td>33.731</td>
<td>13.918</td>
<td>0.254</td>
<td>0.376</td>
<td>0.122</td>
<td>0.578</td>
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<tr>
<td>52</td>
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<td>33.632</td>
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<td>0.251</td>
<td>0.377</td>
<td>0.126</td>
<td>0.590</td>
</tr>
<tr>
<td>51</td>
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<td>33.542</td>
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<td>0.379</td>
<td>0.131</td>
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</table>

### Table 2.5: Effective polarizabilities, Lorentz field factors and orientational order parameter of 4O.3

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>$\alpha_e$</th>
<th>$\alpha_o$</th>
<th>$(\alpha_e - \alpha_o)$</th>
<th>$L_e$</th>
<th>$L_o$</th>
<th>$(L_o - L_e)$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
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<td>37.071</td>
<td>9.177</td>
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<tr>
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<td>47.172</td>
<td>36.509</td>
<td>10.663</td>
<td>0.274</td>
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</tr>
<tr>
<td>76</td>
<td>47.852</td>
<td>36.219</td>
<td>11.633</td>
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<td>0.369</td>
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</tr>
<tr>
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<tr>
<td>72</td>
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</tr>
<tr>
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<td>35.732</td>
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<td>0.371</td>
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<td>35.534</td>
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<td>0.548</td>
</tr>
<tr>
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</tr>
<tr>
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<td>15.021</td>
<td>0.241</td>
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<td>0.594</td>
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<td>0.374</td>
<td>0.137</td>
<td>0.609</td>
</tr>
<tr>
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<td>0.144</td>
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<tr>
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<td>16.356</td>
<td>0.227</td>
<td>0.374</td>
<td>0.147</td>
<td>0.647</td>
</tr>
<tr>
<td>51</td>
<td>51.154</td>
<td>34.648</td>
<td>16.506</td>
<td>0.226</td>
<td>0.374</td>
<td>0.149</td>
<td>0.653</td>
</tr>
</tbody>
</table>
Table 2.6: Effective polarizabilities, Lorentz field factors and orientational order parameter of 1O.10

<table>
<thead>
<tr>
<th>t (°C)</th>
<th>$\alpha_e$</th>
<th>$\alpha_o$</th>
<th>($\alpha_e - \alpha_o$)</th>
<th>$L_e$</th>
<th>$L_o$</th>
<th>($L_o - L_e$)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>54.406</td>
<td>44.069</td>
<td>10.338</td>
<td>0.289</td>
<td>0.358</td>
<td>0.069</td>
<td>0.323</td>
</tr>
<tr>
<td>58</td>
<td>55.336</td>
<td>43.612</td>
<td>11.725</td>
<td>0.284</td>
<td>0.360</td>
<td>0.076</td>
<td>0.366</td>
</tr>
<tr>
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<td>0.384</td>
<td>0.153</td>
<td>0.683</td>
</tr>
</tbody>
</table>

Figure 2.27: Variation of order parameter (S) with $(T_{NI} - T)$ in 4O.2, 4O.3 and 1O.10
Figure 2.28: Variation of $L_e$ with temperature in 4O.2, 4O.3 and 1O.10

Figure 2.29: Variation of anisotropy of Lorentz field factors ($L_o - L_e$) with order parameter ($S$) in 4O.2
Figure 2.30: Variation of anisotropy of Lorentz field factors \((L_o - L_e)\) with order parameter \((S)\) in 4O.3

Figure 2.31: Variation of anisotropy of Lorentz field factors \((L_o - L_e)\) with order parameter \((S)\) in 1O.10
References