ESTIMATION OF ORIENTATIONAL ORDER PARAMETER FROM DIFFERENT MODELS IN 6O.Om LC MATERIALS - AN OPTICAL STUDY

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Abstract

The refractive indices measurements are carried out on a number of Schiff's base 6O.Om compounds with m = 4, 6 to 10 using a wedge shaped cell with a modified spectrometer. The transition temperatures obtained using the POM and DSC are in agreement within the experimental errors. The birefringence data $\delta n = (ne - no)$ along with the density results are employed to estimate the molecular polarisabilty anisotropy, $\delta\alpha = (\alpha e - \alpha o)$ assuming a particular local field (due to Vuks and Neugebauer) the nematic molecule experiences and the order parameter S is estimated from $\delta\alpha$ and $\Delta\alpha$, i.e., polarisabilty anisotropy in the perfect order which is estimated employing different methods. Using these values, the orientational order parameter S has been estimated at

different temperatures in their nematic phase. Further, S can also be obtained from Kuczynski et al. model and also using the effective geometry parameter, αg. Further, it is observed that from our analysis the S value obtained from Δn and αg are identical. The results are analyzed and compared with the body of data available.

1. Introduction

In the field of soft condensed matter physics liquid crystal research play an important role involving the physicists, chemists and technocrats is on the increase due to the importance of these materials in applications especially in display devices and optical switches. It is increasingly dependent on new materials where a chemist is needed and on the physical properties a physicist is essential and for application aspect a technocrat is essential. Further, to understand the fundamental aspects and the usage of liquid crystalline compounds (LCs) in technological applications, the study of physical properties such as density, viscosity, refractive indices, order parameter, S specific heat, etc. will provide more information. A number of people have studied [1-4] the refractive indices of a number of LCs. The orientational order parameter, S can be determined directly from the birefringence following the method of Kuczynski et al. [5], the geometry parameter α_g and the Haller approximation. S value can also be obtained from the polarizabilities following the field methods which are applicable to nematic phase only. The field methods are isotopic Vuks [6] and anisotropic Neugebauer [7] models. In order to calculate the polarizabilities, the density with the temperature is needed. In the perfect order (in the crystalline state), the anisotropy can be obtained semi empirically by following Lippincott et al. [8] and vibrational [9] methods. Then the order parameter, S can be calculated. The advantage of Kuczynski et al. [5] method is no field can be considered and therefore, it can be used to obtain S in cholesteric and smectic phases also.

As a part of systematic studies on N-(p-n-Alkyl benzylidene)-p-n-alkyl anilines (n.m), N-(p-n-Alkoxy benzylidene)-p-n-alkyl anilines (nO.m), N-(p-n-Alkyl benzylidene)-p-n-alkoxy anilines (n.Om), and N-(p-n-Alkoxy benzylidene)-p-n-alkoxy anilines (nO.Om) compounds. The present manuscript gives the detailed investigations of the S value from the polarizabilities and comparing these from those obtained from Kuczynski et al. [5] and the other two methods. In the above n.m, nO.m, n.Om, and nO.Om compounds, the only difference is the placement of electronegative oxygen atom which plays an important role in different ways:

(1) When the oxygen atom is on the left side of the rigid core [on the benzaldehyde side] (nO.m) compounds, generally, the clearing temperatures are below 100ºC. no compound exhibits smectic-I phase, only few compounds show smectic-A to smectic-C (AC) transition [10].

(2) When the oxygen atom is on the right side of the rigid core [on the aniline side] (n.Om), the situation is more or less same as the case of nO.m compounds except in the exhibition of phase variants [1].

(3) When the oxygen atom is on both sides of the rigid core [on benzaldehyde and aniline sides] (nO.Om), the clearing temperatures are elevated to > 100ºC, the presence of nematic phase even in compounds with high alkoxy chain number, and the exhibition of rare phases like smectic-I and the phase transitions like smectic-A to smectic-C (AC), smectic-C to smectic-I (CI) [11-12].

(4) When the oxygen atom is removed from the molecular moiety (n.m), the clearing temperatures are lowered to around 50ºC, the liquid crystalline nature in some cases goes below room temperature and as a result the thermal range of nematic phase is reduced.

The compounds studied in the present manuscript are 4-(hexyloxy benzylidene)-4'-alkoxyanilines of nO.Om series with m = 4, 6 to 10. All these are compared with one another and the body of the data.

2. Experimental

The compounds are synthesized [13] following the standard procedure. The respective 4-hexyloxy benzaldehyde and the corresponding alkoxy anilines are taken in equi-molar proportions in absolute ethanol and refluxed for three to four hours in the presence of few drops of glacial acetic acid which acts as catalyst. After refluxing the reactions for three to four hours, the solvent is removed by distillation under reduced pressure. The crude sample is subjected to repeated recrystallization from absolute ethanol in cold to give the pure compound, until the transition temperatures are constant.

The reaction route for the synthesis of the above compounds is shown below:
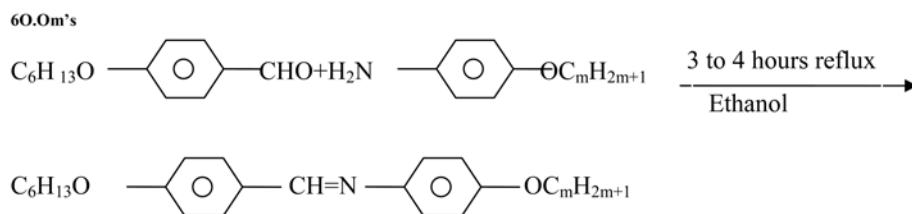
Is the molecular formula of the compounds 6O.Om with m = 4, 6 to 10.

The compounds nO.Om in the present study have the alkoxy chain lengths n = 6 and m = 4, 6 to 10. The compounds with m = 4 and 6 exhibit enantiotropic nematic phase only. The compounds with m = 8 and 9 exhibit a bivariant N-SmC phases while compound with m = 10 shows a trivariant N-SmC-SmI phases. However, the literature data [12] shows that the compounds with m = 7 to 9 exhibit enantiotropic SmC only. The compound with m = 10 as usual exhibits enantitropic SmC and SmI is seen in POM only. The heats of transitions and transition temperatures, observed by DSC and polarizing 3 to 4 hours reflux Ethanol microscope are in good agreement with the literature data. The solid-solid transitions are observed in POM only for the cases of m = 7 to10.

The authors are not able to observe the SmC in 6O.O7 compound in DSC. The authors are able to observe density measurements using density block [14] with very much reduced nematic range. The transition temperatures of the compounds studied are compared with reference 12 in the following way:

(1) In the case of the material 6O.O10 in reference 12 the SmI observed only in POM while in our case we observed in DSC as monotropic transition.

(2) All the phases shown in reference 12 are observed in POM in our case also. The transition temperatures are in agreement within the experimental errors from the literature data [12].

The n_e and n_o values are obtained using a modified spectrometer [15]. The variation of refractive indices with temperature for all the compounds are given in Figures 1 to 6. The wavelength used in the present study is 5893Å.
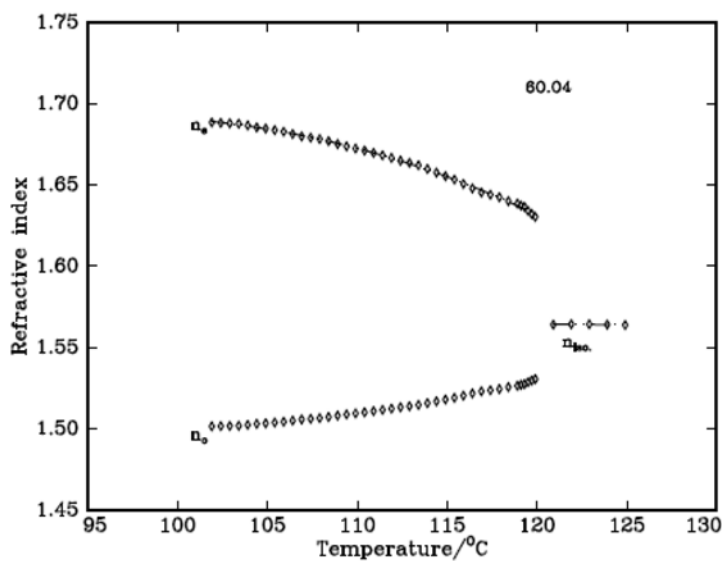

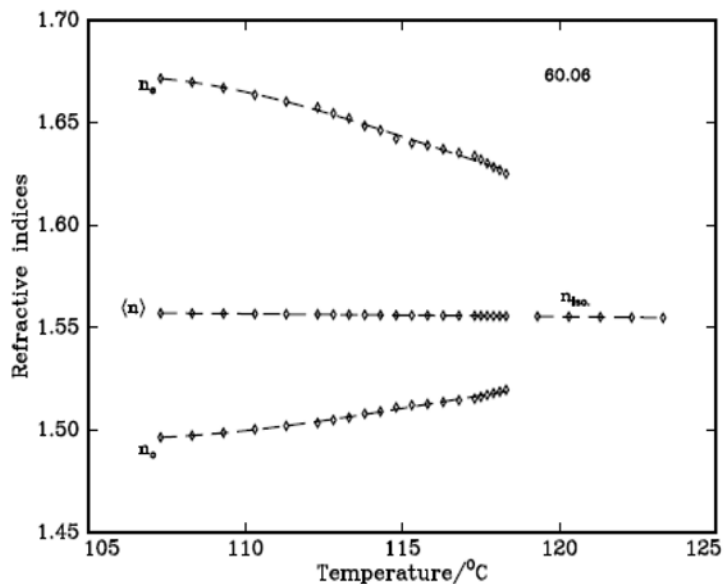**Figure 1.** Variation of n_e, n_o with temperature in 6O.O4 compound.

Figure 2. Variation of n_e, n_o with temperature in 6O.O6 compound.

Figure 3. Variation of n_e, n_o with temperature in 6O.O7 compound.

Figure 4. Variation of n_e, n_o with temperature in 6O.O8 compound.

Figure 5. Variation of n_e, n_o with temperature in 6O.O9 compound.

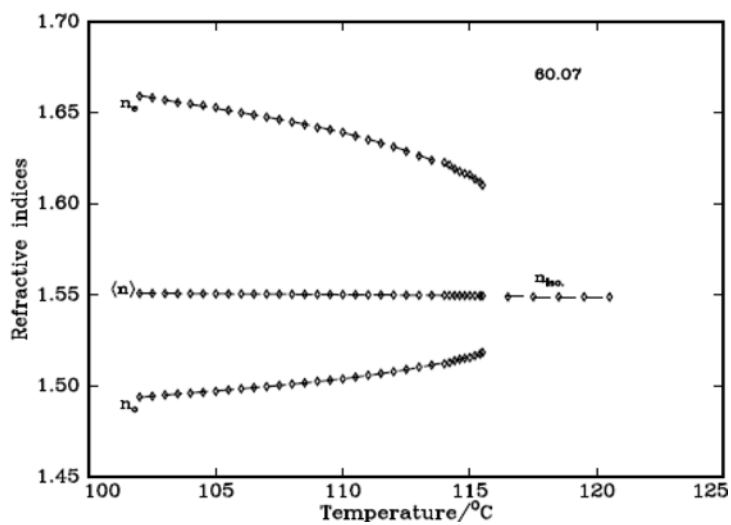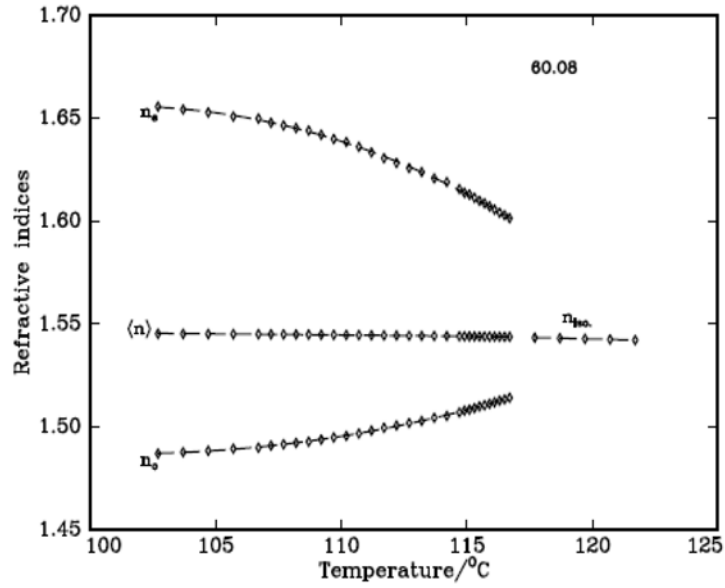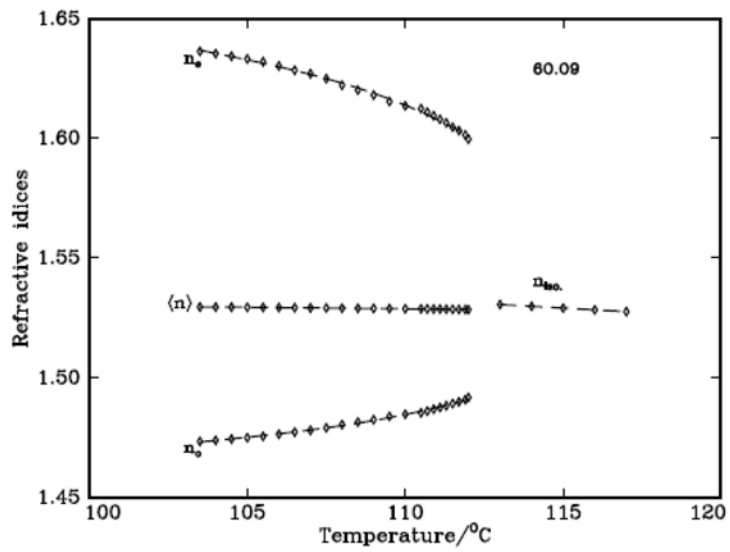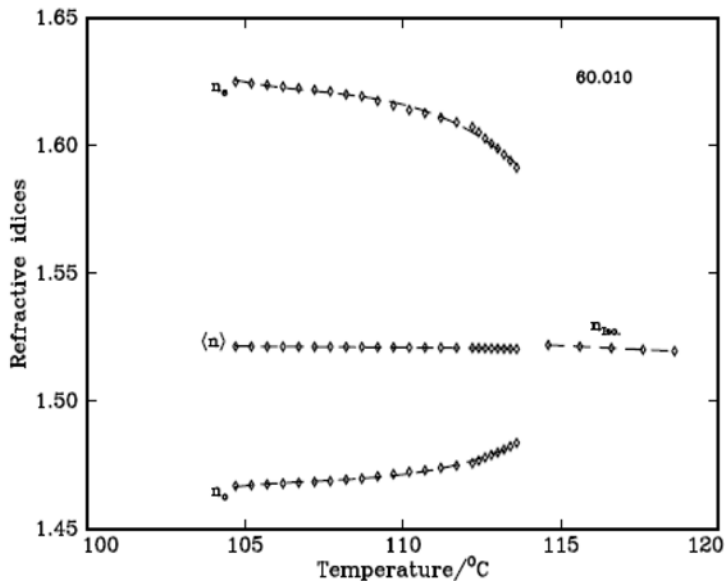**Figure 6.** Variation of n_e, n_o with temperature in 6O.O10 compound.

3. Results and Discussion

The refractive indices [15] are measured for the six 6O.Om compounds. It is observed that the value of refractive index (n_{iso}) is almost constant in the isotropic phase, and with the decrease of temperature from isotropic to nematic phase, at the IN phase transition, the isotropic refractive index value splits into two, extraordinary refractive index $(n_e > n_{iso})$ and ordinary refractive index $(n_o < n_{iso})$, respectively. This splitting is clearly observed in the telescope of the modified spectrometer at the position of angle of minimum deviation at the IN transition. When the temperature is further decreased, the n_e increases while the n_o decreases slightly with further decrease of temperature, in the deep nematic region, the refractive index values of both n_e and n_o saturate.

The order parameter is calculated utilizing different models and they are

(I) S from birefringence, δn.

(II) S from effective geometry parameter, αg.

(III) S calculated by using polarisability anisotropy calculated by using Haller approximation method and the molecular polarisabilities obtained using Neugebauer model.

(IV) S calculated by using polarisability anisotropy calculated by Lippincott δ-function [16] method and the molecular polarisabilities obtained from Vuks model.

(V) S from Vuks scaling factor.

(VI) S from polarizability anisotropy calculated by using molecular vibration [17, 18] method and the molecular polarizabilities obtained by using Vuks model.

(VII) S from polarisability anisotropy calculated by using Haller approximation method and the molecular polarisabilities obtained by using Vuks model.

(VIII) S calculated by using polarisability anisotropy calculated by Lippincott δ-function method and themolecular polarisabilities obtained from Neugebauerb model [19].

(IX) S from Neugebauer $f(B)$ parameter.

(X) S from polarisability anisotropy calculated by using molecular vibration method and the molecular polarisabilities obtained by using Neugebauer model.

Further, the experimental results of refractive indices obtained using wedge technique and the density values are used to estimate the molecular polarisabilities α_e and α_o. The expressions used for the estimation of molecular polarisabilities αe and αo assuming Vuks and Neugebauer internal field models and the estimation of order parameter S are presented in detail in the following sections.

3.1. Calculation of S from birefringence, δn

The $\delta n = (n_e - n_o)$ for all the compounds is drawn with reduced temperature is shown in Figure 7. de Gennes [20] stated that the anisotropy of any physical quantity can be measured from S. In the case of uniaxial LC, this parameter can be defined as

$$Q = \delta A \, / \, \Delta A, \tag{1}$$

where Q is a macroscopic order parameter and δA is the anisotropy of any arbitrary physical quantity, $\Delta A = (A_{\parallel} - A\perp)$ and ΔA is the hypothetical anisotropy of A in the case of perfect order.
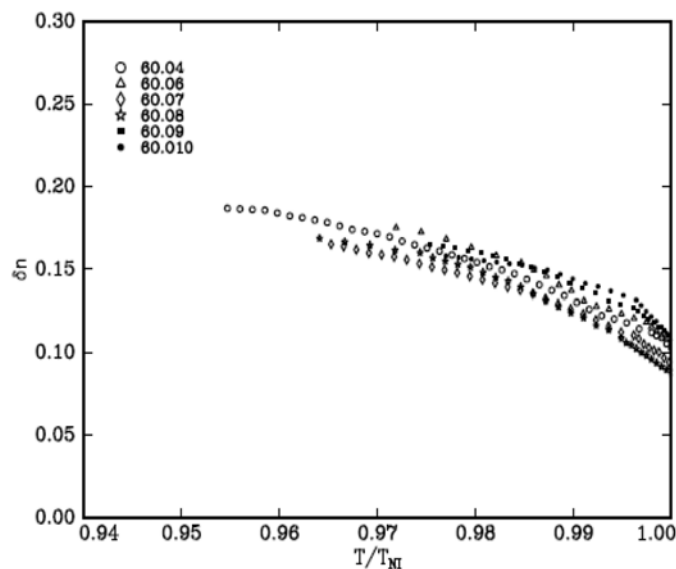

Figure 7. Variation of δn values with reduced temperature $(T \, / \, T_{NI})$ in all compounds.

Kuczynski et al. [5] proposed a simple procedure for obtaining the order parameter S from the birefringence measurements δn without considering the local field experienced by the molecule in a LC phase. The birefringence δn which is a function of temperature is fitted to the following equation:

$$\delta n = \Delta n \left(1 - \frac{T}{T^*} \right)^{\beta}, \tag{2}$$

where T is the absolute temperature, T^* and β are constants (T^* is about 1-4K higher than the clearing temperature and the exponent β is close to 0.20 and the regression coefficient will be close to 0.99). This procedure enables one to extrapolate δn to the absolute zero temperature.

In practice, the three adjustable parameters T^*, Δn and β were obtained by fitting the experimental data for δn to the following equation written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta \log \left(\frac{T^* - T}{T^*} \right). \tag{3}$$

Thus, Q is given by

$$Q = \frac{\delta n}{\Delta n}. \tag{4}$$

Following the procedure of Kuczynski et al. [5], the authors demonstrated that Q determined in this way describes well the nematic order parameter (microscopic one) and is a good approximation of the order parameter S given by equation

$$S = 1/2 < (3 \cos^2 \theta - 1) >, \tag{5}$$

where θ is the angle between the long axis of the molecule and the director n. In general, the order parameter S, defined by Equation (4), must not necessarily be identical with that defined through other tensorial properties and could be different from the order parameter S defined by the above Equation (5). However, one can expect that within a given local field model, there should be a relation between macroscopic and microscopic order parameters and following the procedure of Kuczynski et al. [5] the authors also demonstrated it using the example of the Vuks model. The details of the procedure and the relevant equations are given in the below references. Therefore $Q = S$, where Q is macroscopic order parameter and S is the microscopic order parameter.

The regression analysis is employed to get the best fit for the three parameters viz., T^* or T_C, Δn and β and the values are given in Table 1 for the compounds studied and R is the regression coefficient. The log-log plot is to obtain the Δn value in the case of 6O.O9 as representative cases are shown in Figure 8.

Table 1. Parameters for the best fit through linear regression using Equation (3)

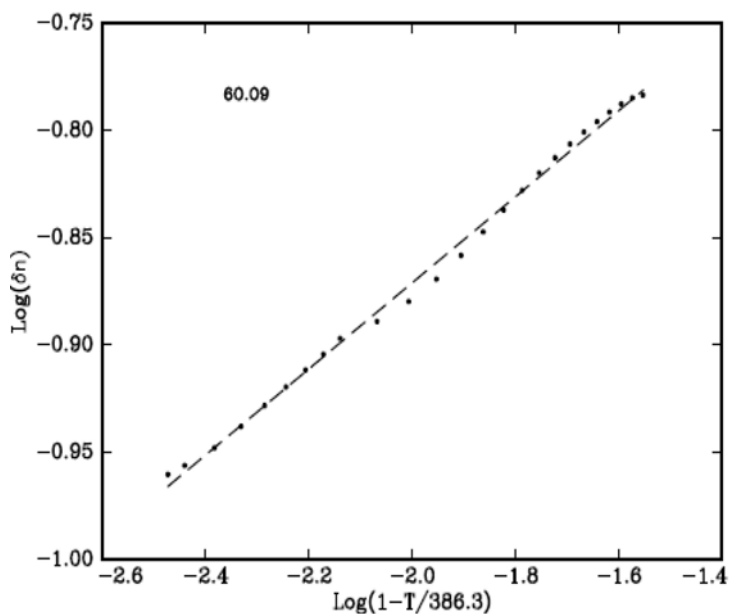| Compounds	T_C	T_{C+}	$\beta \pm 0.002$	Δn	R
6O.O4	392.5	392.5+1.2	0.199	0.342	0.9839
6O.O6	391.3	391.3+1.4	0.203	0.330	0.9862
6O.O7	386.6	386.6+0.6	0.200	0.312	0.9943
6O.O8	389.7	389.7+0.3	0.199	0.316	0.9789
6O.O9	385.0	385.0+1.3	0.200	0.342	0.9983
6O.O10	386.2	386.2+1.8	0.201	0.344	0.9849

Figure 8. Log-log plots for δn with reduced temperature in 6O.O9 compound.

The S values evaluated using the obtained Δn for all the compounds. The advantage of this method is that the S value can be obtained in other liquid crystalline phases like smectics also as no internal field is considered in evaluating the Δn, the birefringence in perfect order.

However, one can expect that within a given local field model, there should be a relation between Q and S. It can be demonstrated by using the example of the Vuks model. From the Vuks equation,

$$(n_e{}^2 - 1)/(< n^2 > +2) = 4\pi N\alpha_\parallel / 3, \tag{6}$$

where $\alpha_\parallel$ is the parallel component of the polarizability and N is the number of molecules per unit volume.

One can obtain a relation between δn and $\Delta\alpha$ as

$$\delta n \equiv (n_e - n_o) = \{(4\pi N_A \rho / 3M)^*(< n^2 > + 2)/(n_e + n_o)\}\delta\alpha, \tag{7}$$

where N_A is the Avogadro number, ρ is density, M is molar mass of liquid crystal, and $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$. It is widely accepted that $\delta\alpha$ is a measure of the order parameter, S. The birefringence, $\delta n = (n_e - n_o)$ could be the same measure of S if the proportionality between δn and $\delta\alpha$ is established. It is a known fact that the terms, $< n^2 >$, n_o, n_e are temperature dependent. In order to establish the condition $\delta\alpha \sim \delta n$, the parameter $\rho(< n^2 > +2)/(n_e + n_o)$ must be independent of temperature, although many parameters in Equation (7) are temperature dependent. One can account for the temperature dependence of density using the fact that the molar refraction r (defined A quantity calculated from a function of the refractive index of a substance multiplied by its molecular weight and divided by its density, which can be taken as a measure of the volume occupied by a molecule of the substance) $= M(< n^2 > -1)/ \rho(< n^2 > +2) = 4\pi\alpha N_A / 3)$ is independent of temperature. This property of r is very well fulfilled for liquids and

there is no reason to expect another behaviour in the case of liquid crystals [19]. In this case ρ can be eliminated from Equation (7). Now Equation (7) takes the form

$$\delta n = \{4\pi N_A (< n^2 > -1)/3R(n_e + n_o)\}\Delta\alpha. \tag{8}$$

The Vuks parameter, V is defined as

$$V = (< n^2 > -1)/(n_e + n_o). \tag{9}$$

It should be independent of temperature. However, in above Equation (8), the quantities $< n^2 >$, n_e and n_o are still temperature dependent. In order to test whether V is constant or not, the author has applied Equation (8) for different n_e and n_o values. It is well known that generally these parameters vary between 1.8 to 1.4 in LC materials and they are temperature dependent. In view of this, the parameters n_e and n_o can be replaced by δn and $< n^2 >$, the later quantity is weakly temperature dependent and further using the relations $\delta n = (n_e - n_o)$ and $< n^2 > = (n_e^2 + 2n_o^2)/3$, one can express V as function of these two parameters and is given as

$$V = \{9(< n^2 > -1)/2(\sqrt{9 < n^2 > -2(\delta n^2)}) + \delta n\} = \text{constant}. \tag{10}$$

In order to test the value of V, the author has drawn the Figure 9 for different values of $< n^2 > = 2.3, 2.4$ and 2.5 and δn changes from ~ 0.08 to ~ 0.18. V calculated using these values obtained for the compounds studied are presented. The calculated change in V on an average is $< \pm 1\%$ for all the compounds studied and V can be taken as constant to good accuracy in the case of isotropic Vuks local field model. However, this is not possible in the case of anisotropic Neugebauer field model to get an equation which gives the relation between δn and $\Delta\alpha$.
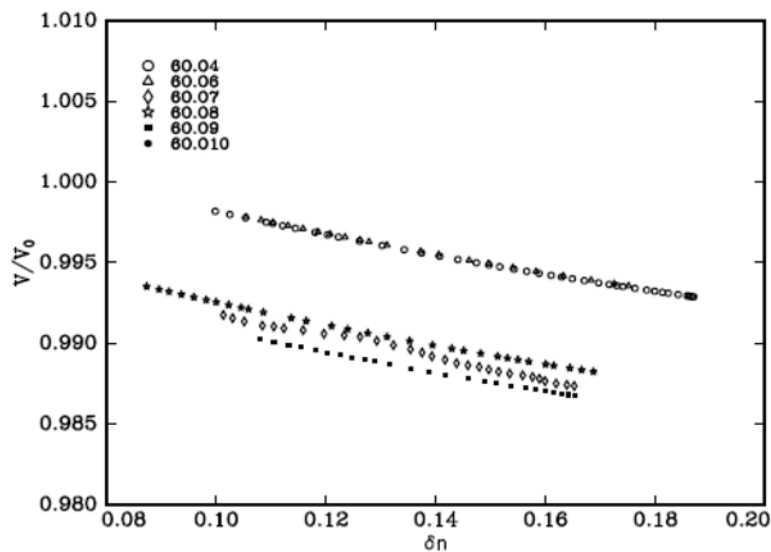
Figure 9. Variation of V / V_o with δn in all compounds.

3.2. Estimation of order parameter 'S' from effective geometry parameter, α_g

The equation for the determination of the order parameter S involving effective geometry parameter [1] $\alpha_g = n_o / n_e$ is given by

$$S = \frac{3\langle n\rangle (1 - \alpha_g)}{[2\alpha_g + 1](\Delta n)_0} ,\qquad (11)$$

Δn_0 is the value at absolute 0.

Where $< n^2 >$ is the average refractive index obtained from the following equation. The simplification of Equation (11) gives rise to Equation (4) only. Hence, no different plot is drawn using (11) for S.

$$< n^2 > = 1 / 3(n_e{}^2 + 2n_o{}^2),$$

which slightly decreases linearly (the decrease is very small) with increase of temperature as follows:

$$\langle n\rangle = C - DT.\qquad (12)$$

The values C and D are obtained by plotting the temperature and average refractive index from above equation by linear regression. The values of C and D are given in below Table 2.

Table 2. The intercept and slope values, C and D, respectively of all the compounds

Compound	C-Value	D-Value
6O.O4	1.604828	-0.0001021
6O.O6	1.571126	-0.0001311
6O.O7	1.561034	$-9.83059E-$
6O.O8	1.589352	-0.0001169
6O.O9	1.569561	-0.0001058
6O.O10	1.529710	$-7.82965E-$

The Figures 10 and 11 show the variation of effective geometry parameter with the temperature and birefringence respectively.

The Figure 10 reveals that α_g increases with the increase of temperature but it decreases with the increases of birefringence linearly and the fit parameters in all the compounds is same within the experimental error with the values (slope -0.061 ± 0.005 and intercept 0.999 ± 0.001). The data is on similar lines and agrees with the literature.
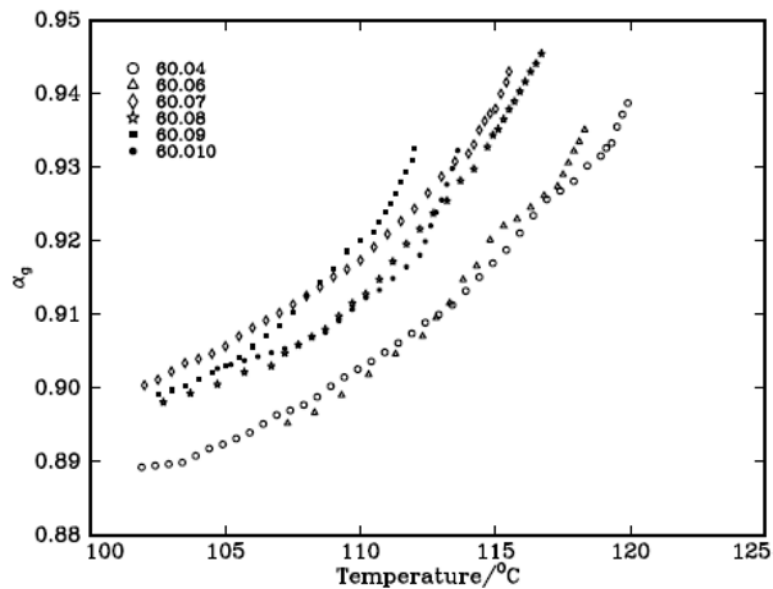
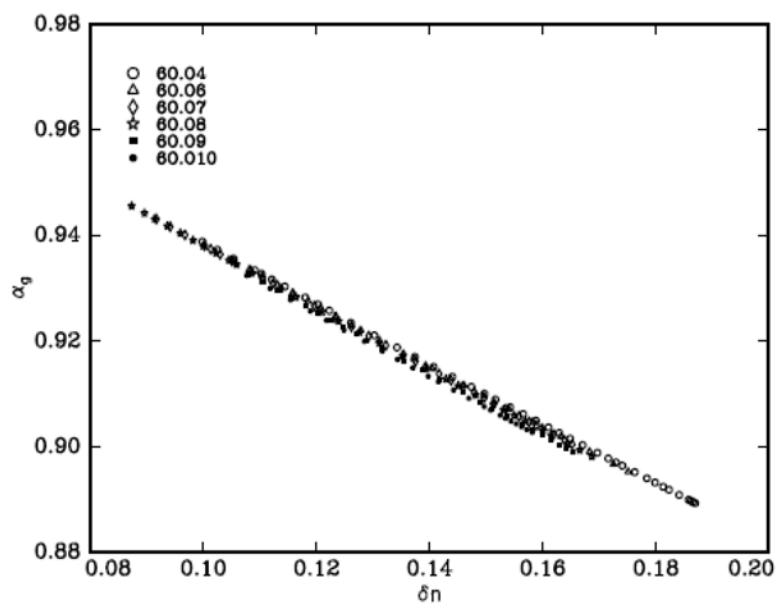**Figure 10.** Variation of α_g with temperature in all compounds.

Figure 11. Variation of α_g with δn in all compounds.

3.3. Estimation of order parameter 'S' from $(1 - T / T_c)^\beta$

The simple method for the determination of order parameter is the Haller et al. [21, 22] equation and is given by

$$S = (1 - T / T_c)^\beta. \tag{13}$$

The variation of order parameter with reduced temperature using Equation (13) is exactly similar to that obtained by using the Equation (4). T_C is the nematic-isotropic transition temperature and β is the material constant. In evaluating the order parameter using the above equation the β values obtained through regression analysis is used. The order parameter S estimated from the above equation for all the compounds with reduced temperature is shown in Figure 12. Further, it is observed that the value of S depends on β.
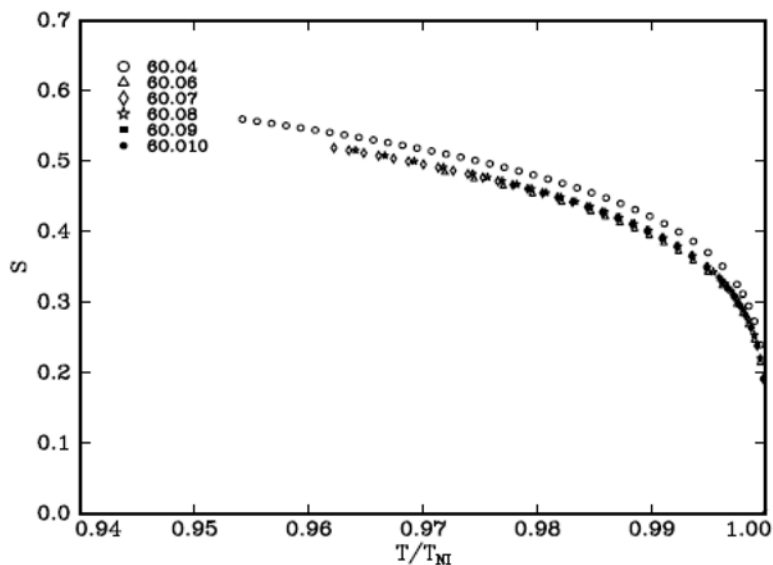

Figure 12. Variation of S estimated with $(1 - T / T_c)^\beta$ with reduced temperature (T / T_{NI}) in all compounds.

3.4. Estimation of order parameter 'S' from polarizabilities

For the estimation of the order parameter S from the molecular polarizabilities α_e and α_o, the following equation is used:

$$S = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp), \tag{14}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the principal polarizabilities and they can be estimated using different methods including the semi empirical methods due to Lippincott et al. [8] and molecular vibration techniques [9]. The two methods are well described. For the sake of compactness, the whole procedures are not described here. Further, the molecular anisotropy can be obtained from the Haller (which is described above) extrapolation technique using the experimentally evaluated molecular polarizabilities from refractive index and density data. The molecular polarizabilities α_e and α_o are evaluated assuming a local field that the nematic molecule experiences. Vuks [6] and Neugebauer [7] proposed two different types of local fields. According to Vuks, the nematic molecule experiences an isotropic field while Neugebauer proposed an anisotropic field to the nematic molecule. The methods used, the expressions employed and the procedures adopted are described below in each case.

3.5. Estimation of molecular polarizabilities from refractive indices and density

The extraordinary (α_e) and ordinary (α_o) polarizabilities corresponding to the electric vector parallel and perpendicular to the optic axis are given

$$\alpha_e = \dot{\alpha} + 2\left(\alpha_\parallel - \alpha_\perp\right)S / 3,$$

as

$$\alpha_o = \dot{\alpha} - \left(\alpha_\parallel - \alpha_\perp\right)S / 3, \tag{15}$$

where S is the order parameter $\alpha_\parallel$ and $\alpha_\perp$ are polarizabilities of the molecule parallel and perpendicular to the long molecular axis of the

liquid crystal molecule. The average molecular polarizability $\overline{\alpha}$ is given as

$$\overline{\alpha} = (\alpha_e + 2\alpha_o)/3 = \left(\alpha_\parallel + 2\alpha_\perp\right)/3. \tag{16}$$

Combining the above two equations S, the order parameter is

$$S = (\alpha_e - \alpha_o)/\left(\alpha_\parallel - \alpha_\perp\right). \tag{17}$$

For the estimation of the molecular polarizabilities of liquid crystal molecules, the authors have considered both the models, one due to Vuks method which considers the local field of the molecule as isotropic and the other due to Neugebauer method which considers the local field as anisotropic. The relevant equations of the two models for the calculation of molecular polarizabilities are given below.

(a) Vuks method

This model was first applied to liquid crystal molecules by Chandrasekhar et al. [23] assuming the internal field as isotropic even in anisotropic crystal. These assumptions lead to the following equations:

$$\alpha_e = \left[\frac{3}{4\pi N}\right]\left[\frac{n_e^2 - 1}{\overline{n}^2 + 2}\right],$$

$$\alpha_o = \left[\frac{3}{4\pi N}\right]\left[\frac{n_o^2 - 1}{\overline{n}^2 + 2}\right], \tag{18}$$

where N is the number of molecules per unit volume, n_e and n_o are the extraordinary and ordinary refractive indices of the liquid crystal molecule.

$$\overline{n}^2 = \left[\frac{n_e^2 + 2n_o^2}{3}\right],$$

and $N = N_A\rho/M$, where N_A is the Avogadro number, ρ is the density, and M is the molecular weight.

(b) Neugebauer method

Subramanyam et al. [24] applied this method to liquid crystal molecule. According to this method, the molecular polarizabilities are

$$\alpha_e = \left(AB - 3 \pm \sqrt{(AB-3)^2 - 4AB} \right) / 2A, \tag{19}$$

$$\alpha_o = \left(AB + 3 \pm \sqrt{(AB+3)^2 - 16AB} \right) / 4A, \tag{20}$$

where

$$A = \frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3} \left[\frac{n_e^2 + 2}{n_e^2 - 1} \right] + \left[\frac{2(n_o^2 + 2)}{n_o^2 - 1} \right], \tag{21}$$

$$B = \left(\alpha_{\parallel} + 2\alpha_{\perp} \right) = (\alpha_e + 2\alpha_o) = 3\alpha = 9\left(\overline{n}^2 - 1 \right) / \left[\left(4\pi N_i \right)\left(\overline{n}^2 + 2 \right) \right], \tag{22}$$

N_i is the number of molecules per unit volume in the isotropic phase. Using the two models, the molecular polarizabilities α_e and α_o of all the liquid crystals are evaluated from the birefringence, $\delta n = (n_e - n_o)$ and density.

The two methods (Lippincott and vibrational) are used to estimate the polarizability components as well as mean polarizabilities for the 6O.Om compounds and the values are given in Tables 3 and 4. The details of the semiemprical calculations due to Lippincott and vibrational are given elsewhere [8, 9].

Table 3. Parallel, perpendicular and mean polarizabilities from Lippincott and molecular vibration methods

Compound	Lippincott			Vibrational method
	$\alpha_{\parallel}^{*}$	$2\alpha_{\perp}$	α_o	α_o
	$10^{-24}\,\mathrm{cm}^3$	$10^{-24}\,\mathrm{cm}^3$	$10^{-24}\,\mathrm{cm}^3$	$10^{-24}\,\mathrm{cm}^3$
6O.O3	79.89	48.56	42.82	43.57
6O.O4	83.54	50.70	44.75	45.54
6O.O6	90.84	54.98	48.61	49.48
6O.O7	94.49	57.12	50.54	51.45
6O.O8	98.14	59.26	52.47	53.42
6O.O9	101.79	61.40	54.40	55.39
6O.O10	105.44	63.54	56.33	57.36

$\alpha_{\parallel n}$ value (1.09) included in parallel component of polarizability

Table 4. Longitudinal $(\sum bL)$ transversal $(\sum bT)$ bond polarizabilities and $\sum b_L - \sum b_I$ from molecular vibration method

Compound	$\sum b_L$	$\sum b_T$	$\sum b_L - \sum b_T$
	$10^{-24}\,\mathrm{cm}^3$	$10^{-24}\,\mathrm{cm}^3$	$10^{-24}\,\mathrm{cm}^3$
6O.O3	64.80	32.96	31.84
6O.O4	67.66	34.48	33.18
6O.O6	73.38	37.52	35.86
6O.O7	76.24	39.04	37.20
6O.O8	79.10	40.56	38.54
6O.O9	81.96	42.08	39.88
6O.O10	84.82	43.60	41.22

The value of S is calculated from the Vuks scaling factor and Neugebauer $f(B)$ parameter and corresponding expressions are given below.

Vuks method (scaling factor)

The order parameter is given by [23, 25]

$$S = \left[\frac{\alpha}{\alpha_\parallel - \alpha_\perp}\right]\left[\frac{n_e^2 - n_o^2}{\bar{n}^2 - 1}\right], \tag{23}$$

where

$$\bar{n}^2 = \left(\frac{n_e^2 + 2n_o^2}{3}\right).$$

Neugebauer method (*f(B)* parameter)

In the Neugebauer method [23], the order parameter S is given

$$S = \left[\frac{\alpha}{\left(\alpha_\parallel - \alpha_\perp\right)}\right]f(B), \tag{24}$$

where

$$f(B) = \left(\frac{9}{4B}\right)\left[\left(B^2 - \left(\frac{10}{3}\right)B + 1\right)^{1/2} + \frac{B}{3} - 1\right],$$

and

$$B = \frac{n^2 - 1}{n^2 + 1}\left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_o^2 + 2}{n_o^2 - 1}\right).$$

The scaling factors for the determination of order parameter are obtained in both the cases by plotting log-log plots between $\left[\dfrac{n_e^2 - n_o^2}{\bar{n}^2 - 1}\right]$ and *f(B)* in Vuks and Neugebauer cases, respectively, against $(T_C - T)/(T_C - T_{NC/NK})$ (where T_C and $T_{NC/NK}$ are clearing and nematic-SmC/nematic - crystal temperatures), i.e., the reduced temperature.

The order parameter, S from the molecular polarizabilities is estimated by assuming Vuks and Neugebauer internal field models. The Figures 13 to 15 represent the variation of order parameter, S with the reduced temperature for the case of 6O.O6, 6O.O8, and 6O.O9 compounds

using the two field models ((a) Vuks and (b) Neugebauer) and the values are compared with the value that is obtained either from δn or α_g, which are identically equal to one another.
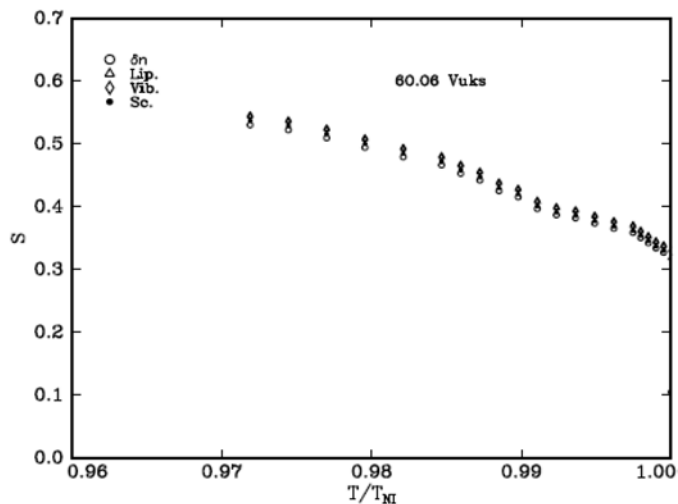

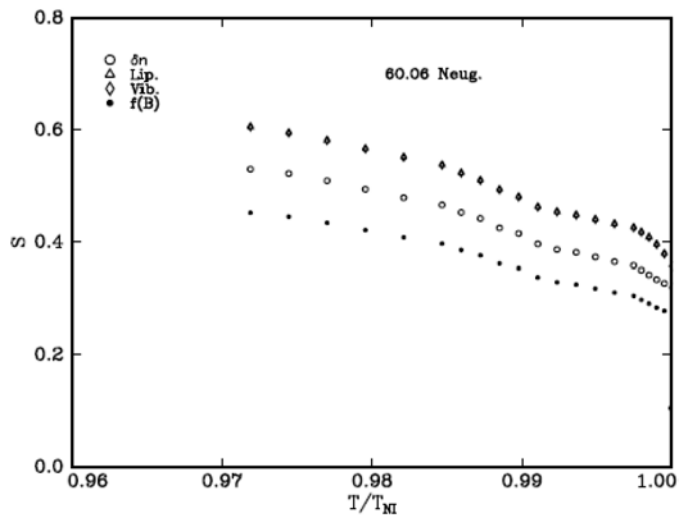**Figure 13(a).** Order parameter, S with reduced temperature for the compound 6O.O6 (Vuks).

Figure 13(b). Order parameter, S with reduced temperature for the compound 6O.O6 (Neugebauer).
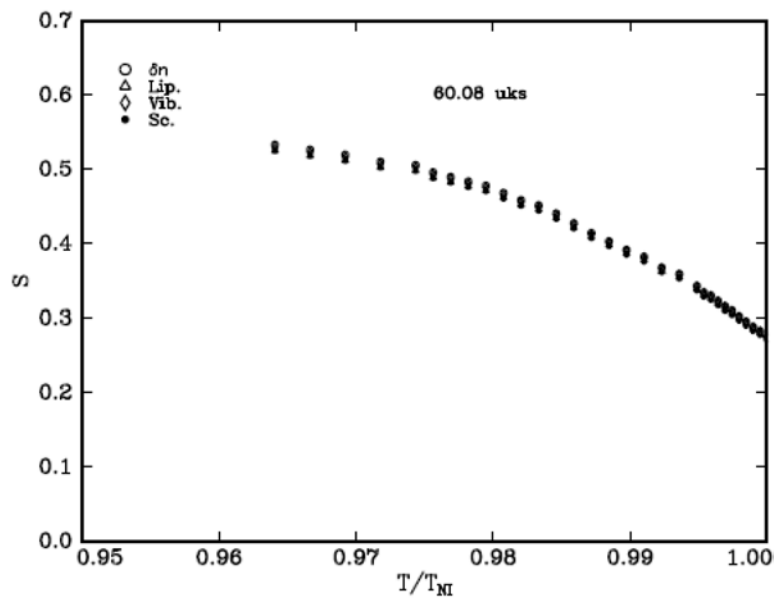
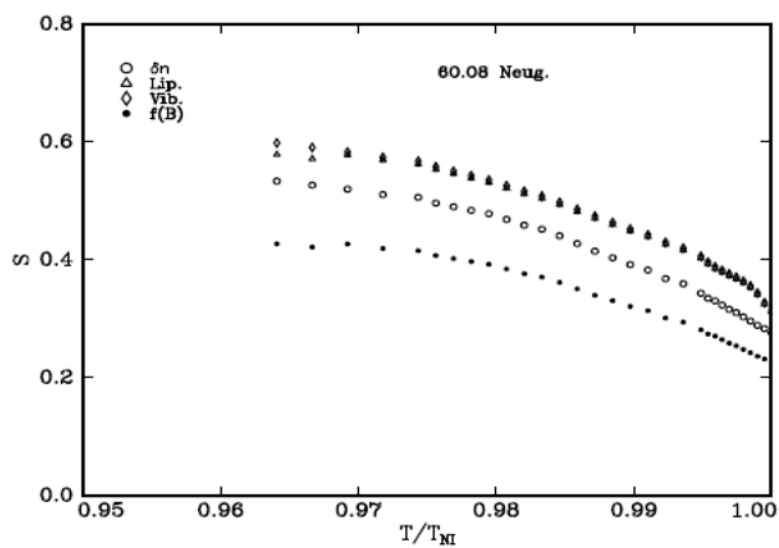**Figure 14(a).** Order parameter, S with reduced temperature for the compound 6O.O8 (Vuks).

Figure 14(b). Order parameter, S with reduced temperature for the compound 6O.O8 (Neugebauer).
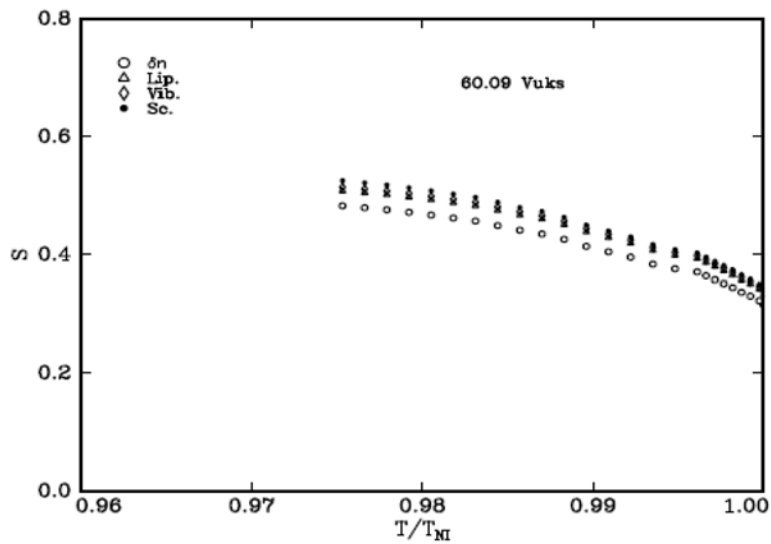
Figure 15(a). Order parameter, S with reduced temperature for the compound 6O.O9 (Vuks).
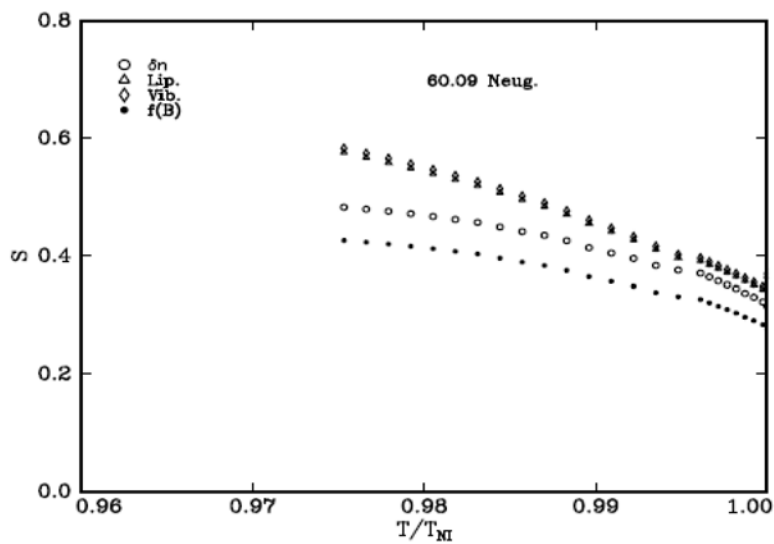

Figure 15(b). Order parameter, S with reduced temperature for the compound 6O.O9 (Neugebauer).

The analysis of obtaining the S is given elsewhere. The authors followed the procedure of Kuczynski et al. [5]. The Table 5 gives the % of deviation of S obtained from $\delta n / \Delta n$, where Δn is the birefringence at perfect order [5, 25, 26]. The deviations are calculated at the middle of the T / T_{NI}. As T / T_{NI} is reached the minimum the deviation in the cases of Neugebauer is more and it exceeds 10%.

Table 5. Percentage of deviations of order parameter, S estimated assuming the two field models and using different methods from that obtained using Δn, the birefringence in perfect order in all compounds

Compound	Vuks			Neugebauer		
	Lip.	Vib.	Sc.	Lip.	Vib.	F(B)s
6O.O4	3.69	3.14	1.99	9.35	8.75	− 5.54
6O.O6	1.26	1.27	0.46	5.57	5.58	− 7.56
6O.O7	− 3.36	− 1.48	− 1.71	6.44	6.44	− 9.06
6O.O8	− 0.63	− 0.25	− 0.81	5.32	5.75	− 8.24
6O.O9	2.56	3.18	4.07	6.77	7.45	− 5.43
6O.O10	3.33	4.12	4.96	6.45	7.29	− 4.66

4. Conclusions

● In all the compounds studied here, with decrease in temperature, n_o decreases while n_e increases, but at a different rate.

● It is observed that α_g increases with increase in temperature, while it decreases linearly with increase in order parameter In either case, it tends toward s unity as the material reaches the clearing point (TC). This is presumably due to increase in the intensity of deflection of light as the material approaches symmetric isotropic state from asymmetric nematic state.

● The values of S estimated from different methods agree well near the nematic-isotropic transition (TC) and diverge as the nematic phase attains equilibrium.

● In the cases where the SmC is present no refractive indices are observed in SmC phase as the splitting has became hazy and the measurement has became difficult.

● The *S* value obtained from the Lippincott δ-function, vibrational method in case of Vuks model agrees in all compounds.

● If the values of percentage errors are compared, it is observed that all compounds exhibit more closeness with the order parameter evaluated from δ*n*.

● Furthermore, the figures reveal that the compounds favor Vuks model than that of Neugebauer model. Even though the order parameter *S* is calculated using by scaling factors of both Vuks and Neugebauer methods also.

However, the values of *S* are always low compared to the above that are obtained using *f*(*B*) parameter of Neugebauer method.

The overall observations from the all compounds suggest the Vuks isotropic model is somewhat favorable to that of Neugebauer model.

Acknowledgements

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