Estimation of Optical Anisotropy and Coefficient of Volume Expansion Of ZLI – 1695 In It'S Nematic Phase

GOLICHA, H.S.A*, MUKHEBI, M.L and SUBRAMAHANYAM, H.S.
Department of physics, Egerton University, P.O. Box 536, Egerton, KENYA.
*Email of the corresponding author: golicha2000@yahoo.com

Abstract

Optical anisotropy and coefficient of volume expansion of ZLI – 1695 (a mixture of 4-n-alkyl-4'-cyanobicyclohexane from E Merck) was calculated using Vuks formula, from refractive indices data determined for the compound. The coefficient of volume expansion β, was also determined. Optical anisotropy was observed to increase with temperature. Also as expected, the value of the coefficient of volume expansion for this nematic phase is lower than those usually observed for ordinary liquids.

Keywords: Liquid crystal displays, nematic, optical anisotropy, coefficient of volume expansion, Vuck's formula,

1 Introduction

Reuter (Reuter 1993) observes that, after their discoveries around the last decade of the nineteenth century, liquid crystals could not find any immediate commercial application. However when they finally did find, about four decades ago, it was with a bang. Today their field of application are as numerous as they are diverse. According to Kelker et al (Kelker and Hatz 1980) these applications range from the electro-optical devices as low power wristwatches to thermometers for clinical observations to applications in thermal imaging techniques useful for night vision. The list is endless.

Another very important application of liquid crystals is their use as anisotropic solvents in which systems of anisotropic solute molecules are studied (Sackmann et al 1974). Such studies range from, those where the liquid crystal is used only as a vehicle in which the properties of the solute molecules are studied as in Nuclear Magnetic Resonance, (Luckhurst and Emsley 1983) to those such as Helical Twisting Power (HTP) involving changes in the host liquid crystals themselves (Kuball and Brunning 1997, Golicha 1999).

One such liquid crystal, commonly used as a solvent for anisotropic solutes is ZLI 1695. This is a mixture of 4-n- alkyl -4-cyanocyclohexanes from Merck of Germany. ZLI 1695 has many unique properties which make it suitable as a solvent. It is a good solvent for most compounds; it has a wide mesomorphic range of temperature (Nematic between 13 ^{0}C-72 ^{0}C). Finally ZLI 1695 does not absorb in the visible and the ultraviolet region, thus making it very suitable for such spectroscopy (Abbate et al 2003).

The use of ZLI 1695 as solvent for anisotropic solvent is fairly widespread. Most of these applications are in guest-host systems where chiral dopants are dissolved as guests in liquid crystalline hosts. In their study on optoelectronic properties of cholesteric liquid crystals, Androchanishvili et al (Chanishvile et al 2005) used as the nematic host for 4-cyano-4-(2-methylbutyl)biphenyl (CB-15 from Merck) and MLC-6248 also from Merck. Malgorzata Marjanska et al (Marjanska et al 2003) dissolved cryptopane-A and chloroform in ZLI 1695 and studied their inclusion complex using carbon 13 NMR. Other researchers (Gyosdosky and Terenetskaya 2002) investigating the dynamics of cholesteric phase induction using steroids as chiral dopants, employed ZLI 1695 as anisotropic solvents.

Solvents have been found to affect the electric and magnetic fields experienced by the molecules placed in them. The magnetic and electric fields experienced by the solute molecules in the presence of the solvent molecules is referred to as the internal or effective fields. (Michl and Thulstrup 1995). The effective magnetic field component is usually equated to that in the vacuum, since the magnetic permeability of non magnetic materials such as the inert solvents is essentially identical to that of the vacuum (Michl and Thulstrup 1995). However the effective electric field component E_{eff} is given as (Michl and Thulstrup 1995);

$$E_{eff} = \alpha'(\tilde{v})E \qquad \text{--}1$$

Where $\alpha'(\tilde{v})$ is the effective polarizability of the solvent and E the applied electric field. This polarizability depends on the wave number $(\tilde{v})$ of the light used.

In the Lorentz approximation, the effective polarizability $\alpha'(\tilde{v})$ of the solvent in the region where the solvent is transparent is related to its refractive index $n(\tilde{v})$ by (Michl and Thulstrup 1995);

$$\alpha'(\tilde{v}) = \frac{\left[n^2(\tilde{v}) + 2\right]}{3} \text{--2}$$

Where $n(\tilde{v})$ is taken as the $n_{ll}(\tilde{v})$ or $n_{\perp}(\tilde{v})$ for measurement with light parallel or perpendicular respectively to the optic axis of the molecule. This leads to the mean principle polarizabilities α_e and α_0 along and perpendicular to the optic axis respectively

There is no denying that the future of liquid crystals is in the display industry (Reuter 1993). In this industry, the difference between the principle polarizabilities (α_e-α_0), also known as optical anisotropy is of paramount interest.

Hence a study of the optical anisotropy and coefficient of volume expansion which are central to the performance of a liquid crystal display (LCD) is expected to shed more light on this important liquid crystalline phase.

Molecular polarizabilities in liquid crystals cannot be measured directly. However some models are known which relate refractive index data to the principle polarizabilities α_o and α_e along and normal respectively, to the optic axis (Hauser et al 1983). Mainly two of these have been used to relate the polarizabilities with the measured refractive indices (Madhusudana 1980). One of these methods, due to Neugbauer (Subramhanyam et al 1974), makes use of anisotropic internal field. The other due to Vuks (Chandrasekhar and madhusudana 1969) assumes an isotropic local field.

It is only natural to suggest that the anisotropic nature of the Lorenz field be taken into account in the determination of the principal polarizabilities, α_e and α_o of these mesophases (Krishnamurti and Subramhanyam 1975), Krishnamurti and Somashekar 1981). However, Dunmur and Munn (Dunmur and Munn 1983) who used this model successfully in their study of nematogens as well as the smectics A and B have reported that the anisotropy of the internal field in liquid crystals is so small that such fields may be considered isotropic, hence allowing the use of Vuks model.

Both of these models have been used successfully on nematic liquid crystals. The model due to Vuks was first applied to the nematic phase by Chandrasekhar and Madhusudana (Chandrasekar and Madhusudana 1969) and later used by many other workers, [e.g. Van Hecke et al 1978, Jen et al 1973, Chang et al 1976, Hauson and shen 1976).

Optical anisotropy

The relationship between the principal polarizabilities and the refractive indices are given by the Vuk's formula as (Hauser et al 1983, Madhusudana 1980, Oshea and Kuster 1981)

$$\alpha_o = \frac{3}{4\pi N}\left(\frac{n_o^2 - 1}{n^2 + 2}\right) \text{---3}$$

$$\alpha_e = \frac{3}{4\pi N}\left(\frac{n_e^2 - 1}{n^2 + 2}\right) \text{--4}$$

Where N is the number of molecules per unit volume of the nematic compound (also called number density), n_o and n_e the refractive indices for the ordinary and extraordinary rays, α_o and α_e are the corresponding polarizabilities and n is the mean refractive index given as:

$$\bar{n} = \tfrac{1}{3}(n_e + 2n_o) \text{---5}$$

Number density, denoted by N, is the number of specified objects per unit volume, given as (Kuzyk 1998);

$$N = \frac{N'}{V}, \text{---6(a)}$$

where N' is the total number of objects in a volume V.

For any substance, the number density N (in units of m^{-3}, cm^{-3} or mm^{-3} etc) can be expressed in terms of its molar concentration C (in units of mole/m^3 , mole/cm^3 or even mole/mm^3) as: (Kuzyk 1998)

$$N = N_A C \text{---------- ---6(b)}$$

where $N_A \approx 6.022\times10^{23}$ mol^{-1} is the Avogadro number.
For atoms or molecules of a well-defined molecular mass M_0 (in units of g/mole), the number density can be expressed in terms of the mass density of a substance ρ (in units of g/m^3) as (Kuzyk 1998);

$$N = \frac{N_A}{M_0}\rho \tag{6(c)}$$

Since the ratio $\frac{M_0}{N_A}$ is by definition, the mas m of a molecule (or atom) of the substance, the units of N the number density is in cm^{-3} if the units of M_0 is g and that of N_A is per mole.

Hence, if n_e, n_o, n and ρ are measured and N is determined as in equation 6(c), then $\Delta\alpha\ (=\alpha_e-\alpha_o)$, the optical anisotropy can easily be determined.

Coefficient of volume expansion
The Electric Susceptibility (χ) values (along and perpendicular to the optic axis of the nematic phase) are given as given as (Chandrasekhar and Madhusudana 1969);

$$\chi_{e,o} = N\alpha_{e,o} \tag{7}$$

Where $\chi_{e,o}$ is the susceptibility corresponding to $\alpha_{e,o}$ and N is the number density as given in equations 6(c). The mean susceptibility $\overline{\chi}$ and the corresponding mean polarizability, $\overline{\alpha}$ are defined as (Van Hecke et al 1978),

$$\overline{\chi} = \tfrac{1}{3}(\chi_e + 2\chi_o) \tag{8(a)}$$

$$\overline{\alpha} = \tfrac{1}{3}(\alpha_e + 2\alpha_o) \tag{8(b)}$$

From equation 7 the mean susceptibility $\overline{\chi}$ is related to the mean polarizability $\overline{\alpha}$ according to the equation;

$$\overline{\chi} = N\overline{\alpha} \tag{8(c)}$$

Where, N (= N' / V) is the number of molecules (N') of the nematic phase per unit volume V.
Substituting for N and taking the natural logarithm of equation 8c, we obtain;

$$\ln\overline{x} = \ln N' - \ln V + \ln\overline{\alpha}\,. \tag{9(a)}$$

Since N' and $\overline{\alpha}$ are temperature independent (Hauser et al 1983), then,

$$\tfrac{\partial}{dT}(\ln\overline{x}) = -\tfrac{\partial}{dT}(\ln V)$$

$$= -\frac{1}{V}\frac{\partial V}{dT}\,.$$

$$\tfrac{\partial}{dT}(\ln\overline{x}) = -\beta \tag{9(b)}$$

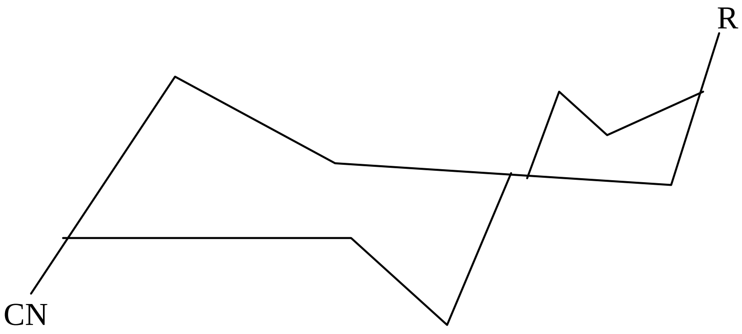
Where β is the coefficient of volume expansion [12], of the nematic phase. Thus on integration we obtain,

$$\ln\overline{x} = -\beta T + C\,. \tag{9(c)}$$

A plot of (- $\ln\overline{x}$) against T should yield a straight line, from which β, the coefficient of volume expansion, may easily be determined.

2 Materials and methods

ZLI 1695 is a mixture of 4 –n-alkyl-4-cyanobicyclohexanes from Merck. The four alkyl groups are C_2H_5, C_3H_7, C_5H_{11} and C_7H_{15}. The structure is given in figure 1.



R = n-C_2H_5
=n-C_3H_7
=n-C_4H_9
=n-C_7H_{15}

Figure 1

Figure 1: Structure of ZLI-1695

The density of ZLI 1695 was determined at different temperatures within the nematic range, using density metre DE 45 DeltaRange. The values of density at different temperatures are given on table 1. The refractive indices at different temperatures were determined using Abbe refractometer. The values of refractive indices at different temperatures are given on table 2. Since the temperatures at which the densities were determined did not correspond to those at which the refractive indices were determined, extrapolation was done to obtain the density at the temperature at which refractive indices data were obtained. This extrapolation is shown on figure 2. Finally from its structure the relative molecular mass of ZLI 1695 was determined, and from equation 6c, the number density (N) was calculated for different densities. Then using the isotropic internal field model due to Vuks (equations 3 and 4) the principal polarizabilities α_e and α_0 and the optical anisotropy $\Delta\alpha(=\alpha_e - \alpha_0)$ were determined at different temperatures. The coefficient of volume expansion was determined from the refractive indices data using equation 9 (c). these values are shown on table 2. Finally the graphs of optical anisotropy and the coefficient of volume expansion are shown on figure 3 and 4 respectively.

temp T (deg. Celsius)	density (g/cm3)	$N = \frac{N_A \rho}{M_w} \times 10^{21}$
20	0.9418	2.06169
22	0.9401	2.05796
24	0.9384	2.05424
26	0.9366	2.0503
28	0.9349	2.04658
30	0.9332	2.04286
32	0.9315	2.03914
34	0.9298	2.03542
36	0.928	2.03148
38	0.9263	2.02775
40	0.9246	2.02403
42	0.9229	2.02031
44	0.9211	2.01637
46	0.9194	2.01265
48	0.9177	2.00893
50	0.916	2.00521
52	0.9143	2.00149
54	0.9125	1.99755
56	0.9108	1.99382
58	0.9091	1.9901
60	0.9074	1.98638
62	0.9057	1.98266
64	0.9039	1.97872
66	0.9022	1.975
68	0.9005	1.97128
70	0.8988	1.96755
72	0.8971	1.96383
74	0.8953	1.95989
16.5	0.944815	2.06829
20.9	0.941029	2.06
24.9	0.937587	2.05246
30.1	0.933112	2.04267
35.6	0.928378	2.0323
44.7	0.920547	2.01516
49.9	0.916072	2.00537
54.5	0.912114	1.9967
59.8	0.907552	1.98671
62.7	0.905057	1.98125
67.2	0.901184	1.97277
71.7	0.897312	1.9643
72.3	0.896795	1.96317
72.6	0.896537	1.9626

Table 1:

T/C	T/T_c	η_e	η_o	$N\times10^{21}$	η	$\alpha_o\times10^{-23}$	$\alpha_e\times10^{-23}$	$\Delta\alpha\times10^{-24}$	$\bar{\alpha}\times10^{-23}$	$\bar{\chi}$	$-\ln\bar{\chi}$	$\Delta\chi\times10^{-3}$
16.5	0.22	1.5339	1.4718	**2.07**	1.4925	3.18	3.69	5.096	3.35	0.069369	2.67	10.5
20.9	0.29	1.5329	1.4709	**2.06**	1.491567	3.19	3.70	5.109	3.36	0.069257	2.67	10.5
24.9	0.34	1.5302	1.469	**2.05246**	1.4894	3.19	3.70	5.061	3.36	0.068997	2.67	10.4
30.1	0.41	1.5278	1.4678	**2.04267**	1.4878	3.20	3.70	4.985	3.37	0.068803	2.68	10.2
35.6	0.49	1.5242	1.4661	**2.0323**	1.485467	3.21	3.69	4.852	3.37	0.06852	2.68	9.86
40	0.55	1.5214	1.4651	**2.02403**	1.483867	3.22	3.69	4.720	3.38	0.068325	2.68	9.55
44.7	0.62	1.5187	1.4633	**2.01516**	1.481767	3.22	3.69	4.665	3.38	0.068071	2.69	9.40
49.9	0.69	1.5149	1.462	**2.00537**	1.479633	3.24	3.68	4.475	3.38	0.06781	2.69	8.97
54.5	0.75	1.5115	1.4609	**1.9967**	1.477767	3.24	3.67	4.298	3.38	0.067581	2.69	8.58
59.8	0.82	1.507	1.4592	**1.98671**	1.475133	3.25	3.66	4.080	3.39	0.067259	2.70	8.11
62.7	0.86	1.5042	1.459	**1.98125**	1.474067	3.27	3.65	3.868	3.39	0.067127	2.70	7.66
67.2	0.93	1.497	1.4579	**1.97277**	1.470933	3.27	3.61	3.358	3.38	0.06674	2.71	6.62
71.7	0.99	1.4902	1.4578	**1.9643**	1.4686	3.29	3.57	2.793	3.38	0.06645	2.71	5.49
72.3	1.00	1.4882	1.4582	**1.96317**	1.4682	3.30	3.55	2.587	3.38	0.066399	2.71	5.08
72.6	1	1.4885	1.4586	**1.9626**	1.468567	3.30	3.56	2.579	3.39	0.066444	2.71	5.06
		clearing point T_C is 72,6 degrees Celsius			72.6							

Table 2

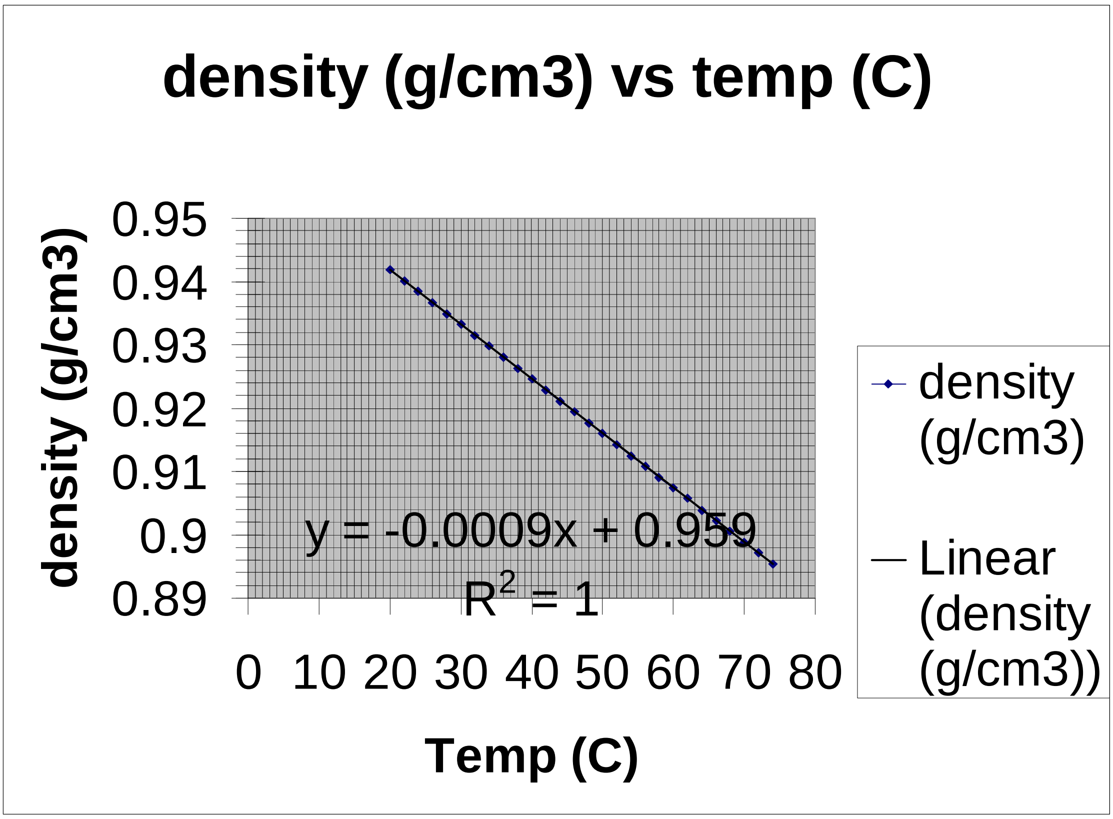


Figure 2: Graph of density against temperature

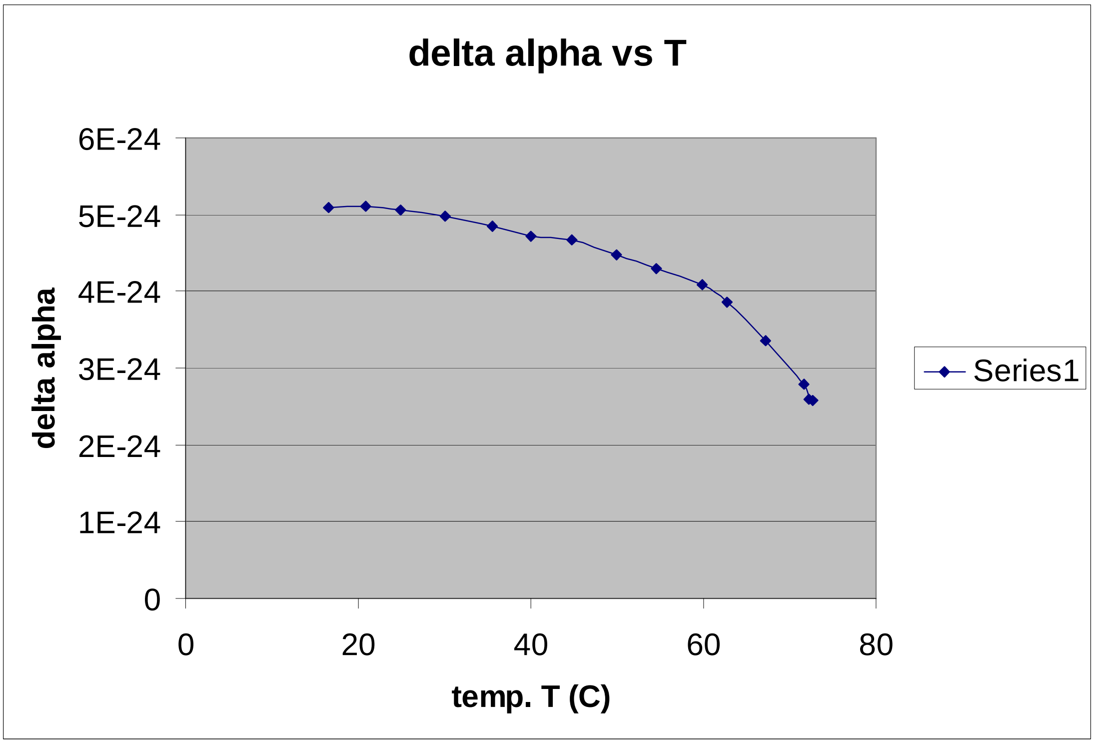


Figure 3: Graph of Δα against temperature

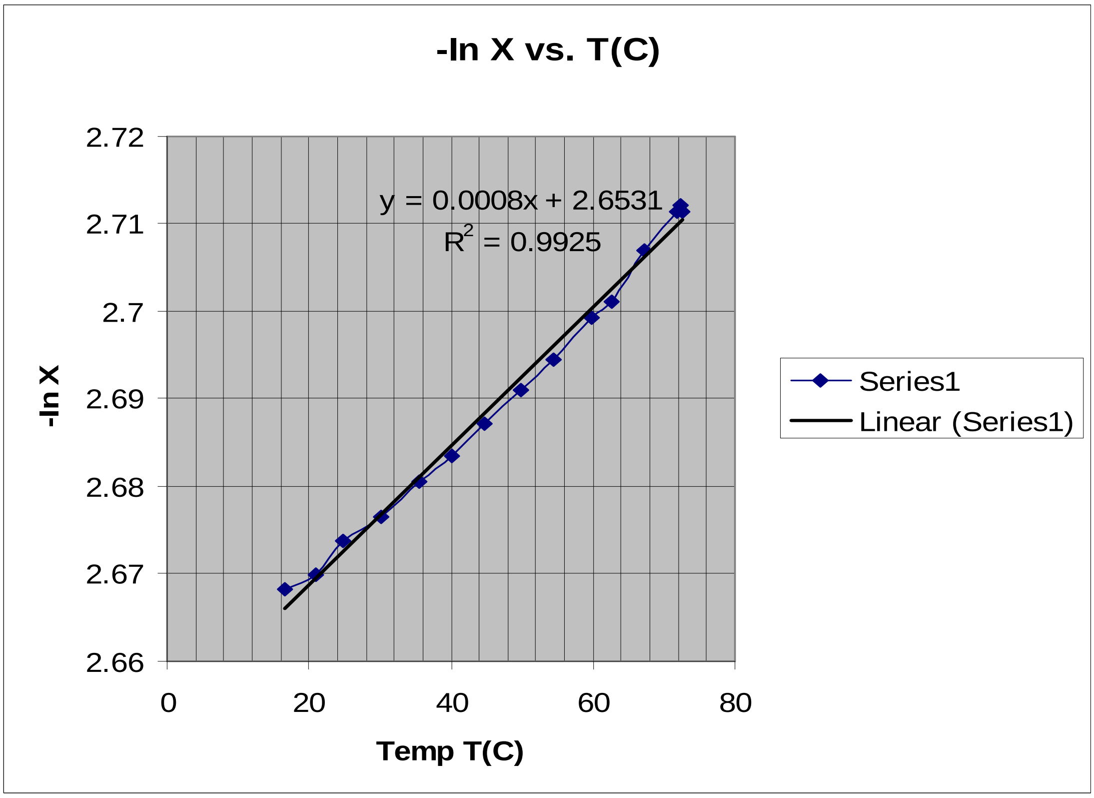
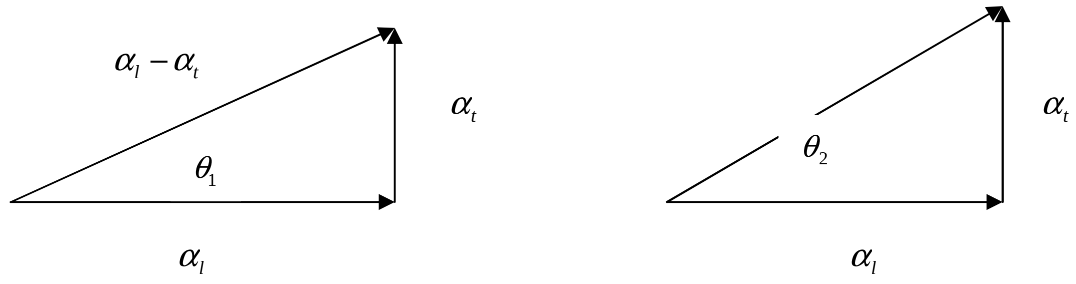


Figure 4: Graph of - lnχ against temperature

3 Results and discussion

Optical anisotropy ($\Delta\alpha$)

Figure 3 shows that, optical anisotropy $\Delta\alpha$, decreases as temperature increases and actually vanishes as the clearing point is approached (at 72.6 ^{0}C). The explanation for this may be found in the activities of the individual molecules. By virtue of the anisotropy of the phase (nematic in this case) the molecule has two principle polarizabilities α_{ll} and $\alpha_{\perp}$, parallel and perpendicular respectively to the optic axis as shown on figure 5(a).



(a) low temperature (b) at higher temperature

Fig 5 Variation of α_l *and* α_t at

One should be careful when using figure 5(a) because it shows polarizability as a simple vector while we know it is a tensor quantity.

Due to thermal agitation, the orientation of the long molecular axis usually fluctuates around the director, making an average angle θ_1 with it. As the temperature increases the fluctuations of these orientation also increases making an average angle θ_2 ($\theta_2 > \theta_1$). This has the effect of reducing α_{ll} while increasing $\alpha_{\perp}$ (Golicha et al 2006). This is clearly shown on figure 5(b).

On the macroscopic scale the corresponding values α_e for α_{ll} and α_o for $\alpha_{\perp}$ are consequently affected. Hence $\Delta\alpha$ (= α_e - α_o) decreases with increase in temperature.

This decrease of $\Delta\alpha$ may also explain the usually observed independence of $\bar{\alpha}$ on temperature. Since with an increase in temperature α_e decreases while α_o increases, (the reverse is the case when temperature is lowered), the mean $\bar{\alpha} = \frac{1}{3}(\alpha_e + 2\alpha_o)$ remains unchanged.

There is also change in density (accompanying the temperature change) which affects the two principle polarizabilities. For the specific case of the Nematic phase which was studied for ZLI 1695 , where the molecules lie parallel to the director, an increase in temperature, hence thermal agitation, affects more the distance between the molecules than the length of the molecules. This causes increase in the packing volume of the molecules, hence a decrease in the density (Golicha et al 2006). Thus both α_e and α_o increase as a result, though it is α_o which increases much more since the increase in the packing volume of the molecules is more from the lateral expansion perpendicular to the optic axis than it is from that parallel to it. Hence $\Delta\alpha$ decreases with temperature.

Coefficient of volume expansion.

The variation with temperature of $-\ln\bar{\chi}$ (shown on figure 4) shows a linear increase with temperature. As already explained, an increase in the temperature causes increase in the packing volume hence a decrease in $\Delta\alpha$. From equation 8(c) $\bar{\chi} = N\bar{\alpha}$. As temperature increases $\bar{\alpha}$ remains constant, as shown on table 2, but N decreases (table 1) due to increase in packing volume. Now as N decreases, $\bar{\chi}$ decreases too (table 2). Hence $\left(\frac{1}{\bar{\chi}}\right)$ increases with increase in temperature, thus ln$\left(\frac{1}{\bar{\chi}}\right)$ increases with temperature. But ln$\left(\frac{1}{\bar{\chi}}\right)$ = ln $\bar{\chi}^{-1}$.= -ln $\bar{\chi}$. Thus -ln $\bar{\chi}$ increases with temperature. Also there is change in packing volume as the temperature increases. However, since the contribution to the change in the packing volume (hence $\bar{\chi}$) of the increase in molecular length (affecting χ_e) is very small compared to that due to the motion perpendicular to it (affecting

χ_o), the change in volume per degree Celsius is almost entirely due to χ_o . This change in packing volume is proportional to the temperature of the mesophase, Hence the rate of change of -ln $\overline{\chi}$ with temperature, representing coefficient of volume expansion is a constant. This is shown by the nearly constant slope of the plot on figure 4.

As may be expected the value of β is somewhat lower than in the case of liquids where the motion of the molecules is less restricted (Halliday and Resnik 1978). In the liquid crystalline phase the molecules have orientational order and only certain motions of the chains are allowed. It may be observed that in the particular case of this liquid crystal (and indeed in most mesophases) the presence of the rigid core may act as a hindrance to the change in the packing volume of the molecules. Hence a lower value of β for this mesophase.

5 Conclusions

Optical anisotropy was observed to increase with temperature. Also as expected, the value of the coefficient of volume expansion for this nematic phase is lower than those usually observed for ordinary liquids.

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