

## Phase Transition and Thermodynamic Parameters of Liquid Crystalline Mixtures – A Dilatometric Study

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**Abstract**— In the present work heptyl amino methyl-hydroxy phenoxy biphenyl carbonitrile Liquid crystals of spacer length  $n=6, 7$  and hexyloxy benzylidene amino phenyl benzoates of terminal group  $m=10, 13$  are chosen. Each of the above two series of compounds are taken in equal concentration and their mixtures C1 and C2 are prepared. The transition temperatures and optical textures of these mixtures are recorded by using polarizing optical microscope. The temperature variation of density is measured by dilatometer. The density and thermal expansion coefficient results reveals that the mixture C1 exhibits nematic, smectic A and smectic B phases, the mixture C2 exhibits only nematic and smectic A phases. The temperature dependence of number of thermodynamic parameters viz., Moelwyn-Hughes parameter, Beyer's nonlinearity parameter, the reduced molar volume, Sharma parameter, fractional free volume, isothermal, isobaric, isochoric Gruneisen parameters etc., are estimated. The results reveal that all the thermodynamical parameters show characteristic changes in the vicinity of phase transformation. The results are discussed based on the data obtained.

**Keywords**—Liquid crystalline mixtures, optical textures, phase transitions, density, thermal expansion coefficient and thermodynamic parameters.

### I. INTRODUCTION

Liquid crystals are self-assembled dynamic functional soft materials which possess both order and mobility at molecular, supra molecular and macroscopic levels [1-2]. Many applications of liquid crystals rely on their physical properties such as phase transitions, order parameter, thermodynamic parameters and also the nature of their response to external perturbations[3-4]. The observation of optical texture change in the optical microscope has usually been the first technique employed to identify the phase transition temperature of any system. However it has to be acknowledged that this is a subjective and qualitative approach. An objective and quantitative technique would be valuable. Accordingly the density studies involving temperature variation and across different phase transformations in LC materials are well known [5-8] to provide information regarding the nature of phase transformation and the growth of pre-transitional effects. Such studies provide complementary and confirmatory experimental evidence for the results

obtained by using other techniques like DSC (differential scanning calorimeter).

With technological advances the liquid crystal display is now a days expects to achieve high electro optical performance as well as to be of low power consumptions [9]. Instead of synthesizing a number of high quality liquid crystal compounds as constituents for suitable mixtures can be used in display. By mixing two nematogens. one can often obtain a lower melting point. Usually, two nematogens exhibit the property of continuous miscibility without crossing any line [10]. Binary mixtures offer the advantage of frequently exhibiting eutectic behaviors in their solid-mesophase transition and in mesophase isotropic transition the temperature varies linearly with composition. Further for technological use of liquid crystals, the liquid crystalline materials of specific molecular design and synthesis are viable but expensive to influence the properties of mesophases. The needed properties can be reached by mixing compounds with various molecular

shapes and properties rather than by looking for pure compounds [11-12]. Miscibility studies are still in their infancy [13-17]. Following this reason, we have studied the mixture of some novel liquid crystals.

## II. RELATED WORK

The liquid crystal research is a part of material work which consists of the design, synthesis and characterization of new novel materials. The next step is to test their suitability in applications by measuring different physical and optical properties. In this work we have exploited phase transition and various thermo dynamical parameters on above liquid crystalline mixtures. The thermodynamic parameters shows abrupt changes at the vicinity of phase transition.

## III. MATERIALS AND METHODS

The Liquid crystal mixture C1 is prepared by weighing 4'-(6-(4-(heptylamino)methyl)-3-hydroxyphenoxy)hexyloxy)biphenyl-4-carbonitrile and 4((4(hexyloxy)benzylidene)amino) phenyl 4-(decycloxy)benzoate in equal ratio by using electronic balance. The compounds are mixed and dissolved in ethyl alcohol. The solution is slowly heated above its clearing temperature by placing it in ultrasonic sonicator. Then the mixture is cooled in desiccator until the ethyl alcohol is completely evaporated. The dry liquid crystal mixture is used for present studies. Similarly C2 is prepared by taking 4'-(7-(4-(heptylamino) methyl)-3-hydroxyphenoxy)heptyloxy)biphenyl-4-carbonitrile and 4-((4-(hexyloxy)benzylidene) amino)phenyl 4-(tridecycloxy)benzoate. The transition temperatures of mixtures C1 and C2 and their optical textures are represented in table 1 and Figs.1-5.

**Table. 1 The Transition temperature( $^{\circ}$ C) of the liquid crystalline mixtures**

Compound	Transition Temperature $^{\circ}$ C				Thermal range		
	I-N	Sm A	Sm B	Cryst al	$\Delta$ N	$\Delta$ Sm A	$\Delta$ Sm B
C1	184.	169.	160	85.6	15.	9.1	74.4
	6	1			5		
C2	139	109	---	67.1	30.	41.9	--
					0		

### Mixture C1:



Fig.1 Nematic at 184  $^{\circ}$ C



Fig. 2 Sm A at 169.1  $^{\circ}$ C



Fig. 3 Sm B at 160  $^{\circ}$ C

### Mixture C2:



Fig.4 Nematic at 139  $^{\circ}$ C

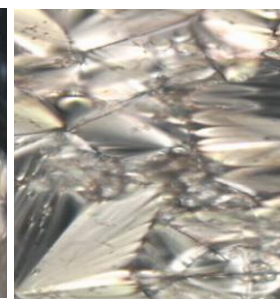


Fig. 5 Sm A at 109  $^{\circ}$ C

The density of liquid crystalline mixtures is measured by using dilatometer, which consists of specially made pyknometer. The pyknometer consists of capillaries of diameter about 250 $\mu$ m and 7-12 cm length is mounted on a U- shaped glass tube. The pyknometer is calibrated by measuring the molar volume of water at different temperatures. The LC mixture is filled in pyknometer and kept in the heating chamber at a temperature of 5  $^{\circ}$ C above the clearing temperature, then the sample is slowly cooled until the sample level reaches the mark in

capillaries. The excess sample in the cups of the capillaries is removed by syringe. The main scale and Vernier scale is replaced with a digital scale instead of viewing the liquid level through the eyepiece of telescope. A charge coupled device camera is attached to the telescope and the levels of the sample in the capillary were observed on a monitor with high accuracy.

The density of LC mixtures is found to decrease with the increase of temperature except in the vicinity of phase transitions where it shows a steep increase, before it attains equilibrium value of the next (lower temperatures) phase. The density jump,  $(\Delta\rho/\rho)$  is calculated as the vertical distance between the density values ( $\rho_1$  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.,  $\frac{(\rho_1 - \rho_2)}{(\rho_1 + \rho_2)/2}$ . The observed density jump  $(\Delta\rho/\rho)$ , the thermal expansion coefficient maxima  $(\alpha)_{max}$  and density slopes across different phase transitions are presented in the tables 2-4.

**Table.2 Percentage of density jumps in different phases of LC mixtures**

Compound	Phase variant	% of $\Delta\rho/\rho$ <sub>I-N</sub>	% of $\Delta\rho/\rho$ <sub>N-SmA</sub>	% of $(\Delta\rho/\rho)$ <sub>SmA-B</sub>	% of $\Delta\rho/\rho$ <sub>Cr</sub>
C1	N-A-B	0.3256	0.3036	0.2223	0.1872
C2	N-SmA	0.2556	0.1934	---	0.1705

**Table.3 Thermal expansion coefficient maxima  $(\alpha)$  in different phases of liquid crystalline mixtures**

Compound	Phase variant	$(\alpha)_{I-N}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(\alpha)_{N-SmA}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(\alpha)_{SmA-B}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(\alpha)_{cry}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$
C1	N-A-B	30.1	28.5	21.1	19.2
C2	N-SmA	24.1	18.9	---	17.5

**Table.4 Density slopes in different phases of liquid crystalline mixtures**

Compound	Phase variant	$(d\rho/dT)_{iso}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(d\rho/dT)_N$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(d\rho/dT)_S^{mA}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$	$(d\rho/dT)_S^{mB}$ $\times 10^{-4} \text{ } ^\circ\text{C}^{-1}$
C1	N-A-B	6.126	8.5	9.7	10.1
C2	N-SmA	10.5	11.1	11.6	---

The theory for the estimation of different thermodynamic parameters using the coefficient of thermal expansion ( $\alpha$ ) is reported by several authors [18-19]

The Moelwyn-Hughes parameter [20] Beyer's nonlinearity parameter and the reduced molar volume ( $\tilde{V}$ ) are evaluated from the following expressions.

$$C_1 = \frac{13}{3} + (\alpha T)^{-1} + \frac{4}{3}(\alpha T)$$

(1)

$$B/A = C_1 - 1$$

(2)

$$\tilde{V} = \left[ 1 + \frac{\alpha T}{3(1+\alpha T)} \right]^3$$

(3)

Using the coefficient of thermal expansion Haward and Parker [21] obtained an expression for the isochoric temperature coefficient of internal pressure (X) as

$$X = \frac{-2(1+2T)}{V C_1}$$

(4)

The Sharma parameter ( $S_o$ ) [22-23] is given by the expression

$$S_o = \frac{-X}{2} (3 + 4\alpha T)$$

(5)

The isothermal microscopic Gruneisen parameter ( $\Gamma$ ) is a measure of volume dependence of the harmonicity of the normal mode frequency ( $\nu$ ) of a molecular vibrations of a polymer and is related to Fand  $S_o$  as

$$\Gamma = \left(\frac{2}{3}\right) \alpha T + \left(\frac{2+F+4\alpha T}{2\alpha T}\right)$$

(6)

The fractional free volume (f) is a measure of disorder due to increasing mobility of molecules in a polymer and can be expressed in terms of the isothermal microscopic Gruneisen parameter ( $\Gamma$ ) as

$$f = \left(\frac{V_a}{V}\right) = \left(\frac{1}{\Gamma+1}\right)$$

(7)

Where  $V_a$  is the available volume of a liquid crystal.

Thermal parameter ( $A^*$ ) is a dimensionless parameter which shows that at low temperatures, a liquid crystal tends to be ordered exhibiting a small thermal expansion and small fractional free volume, thereby making  $A^*$  equal to unity.

$$A^* = \left(\frac{1+f^2}{1-f}\right) = 1 + \left(\frac{f}{\Gamma}\right)$$

(8)

The Gruneisen parameter ( $\Gamma_p$ ) for liquid crystals can be found from

$$\Gamma_p = \left(\frac{2}{3}\right)\alpha T + \left(\frac{1}{2\alpha T}\right) + 2 \quad (9)$$

The isothermal, isobaric and isochoric Gruneisen parameters are identical to the corresponding acoustical parameters so one can write

$$\Gamma_{ich} = \Gamma_{ith} + \Gamma_{iba} \quad (10)$$

The isochoric Gruneisen parameter  $\Gamma_{ich}$  could be evaluated using the following equation

$$\Gamma_{ich} = -\frac{E-F}{F} \quad (11)$$

Where  $E = -[2 + (\alpha T)^{-1}] \left[ 2\alpha(\bar{V})^{C1-1} \right]$  and  $F = -2\alpha$

The Huggins parameter (F) of a liquid crystal is related to  $S_0$  by the equation

$$F = 2 \left[ 1 + \left( \frac{S_0}{3+4\alpha T} \right) \right] - \left( 3 + \frac{4\alpha T}{3} \right) \quad (12)$$

The isothermal Anderson-Gruneisen parameter  $\delta$  is known to be an important parameter in the theory of temperature dependence of bulk modulus in solids. It is defined as

$$\delta = 2\Gamma_{iba} \quad (13)$$

The Anderson-Gruneisen parameter is distinguished from the Moelwyn-Hughes parameter by introducing a new parameter  $\theta$  as

$$\theta = 2(\Gamma_{ith} - \Gamma_{iba}) + 1 \quad (14)$$

#### IV. RESULTS AND DISCUSSION

##### Isotropic-Nematic (IN) transition:

The isotropic to nematic transition is accompanied by the density jumps of 0.3256 and 0.2556 and the respective thermal expansion coefficient maxima  $(\alpha)_{max}$  across this transitions are  $30.1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ , and  $24.1 \times 10^{-4}$ . The percentage of density jumps is within the range of 0.2 to 0.4 of the values reported [24] in literature across isotropic - nematic interface

The slopes of the density variation with temperature  $(dp/dT)_{iso}$  in the equilibrium isotropic phase for mixtures is  $6.126 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  and  $10.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ , similarly the values of density slopes in nematic phase

is  $8.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  and  $11.7 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  for C1 and C2 respectively.

The distinct values of density jumps, thermal expansion coefficient maxima and density slopes suggest that the IN transition nature is first order and are found to be in agreement with the body of the data available on number of LC compounds [25-27]. The higher values of density slopes in equilibrium nematic phase than the isotropic phase indicates the molecular packing in the nematic phase and accompanying growth of long range orientational order from a completely disordered molecular arrangement in the isotropic phase.

##### Nematic-Smectic-A (NA) transition:

The nematic-smectic-A (NA) transition is observed in liquid crystalline mixtures C1 and C2. The density jumps and thermal expansion coefficient maxima and density slope value in case of M1 is 0.3036,  $28.50 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  and  $8.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . These values suggest that the transition is first order. This particular aspect is further supported by the value of McMillan parameter ( $M = T_{NA}/T_{IN}$ ) is 0.9160 which is above the value of 0.87 predicted from the McMillan theory [27] for a possible first-order transition. Whereas the density jumps, thermal expansion coefficients maxima and density slope obtained in C2 is 0.1934,  $18.9 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  and  $11.1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . The percentage of density jump is smaller compared to number of LC compounds [24-26]. This transition is a peculiar one as it exhibits second-order transition. This feature is supported by the value of McMillan parameter ( $M = T_{NA}/T_{IN}$ ) is 0.7841 which is less than 0.87 predicted from McMillan theory for a possible second order transition.

The density slope values in SmA transitions are higher compared to those obtained in Nematic and Isotropic phases and this higher values suggests an additional packing if the molecules with positional and translational order in SmA phase.

##### Smectic-A to Smectic-B (AB) transition:

The smectic-A to smectic-B transition is observed only in mixture C1. The density jump, thermal expansion coefficient maxima and density slope across this transition is 0.223,  $21.1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  and  $10.1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . The density jump is small compared to those observed in other pure compounds. The density increases linearly from SmA to SmB phase with a finite slope. Further, the observation of the presence of two phase co-existence for small temperature range co-terminates with the bordering of transition. Hence, the broadening

is explained due to a two phases co-existence which occurs commonly and does not require pre-transitional effects like Sm-C to Sm-B transition. Further, more the transition involving positional disorder molecular arrangement in Sm-A layers to positional ordering in Sm-B phase might be the origin of two phase co-existence. Although, it is conceivable that impurities can convert an otherwise second order transition into a first order transition, there is absolutely no reason to believe that this effect is occurring here. For example, the complete absence of pre-transition phenomenon expected for second or weakly first order transitions weighs heavily against any such hypothesis.

The higher values of density slope when compared to isotropic, Nematic and smectic-A phases suggest that the crystalline smectic-B phase has a long range three dimensional order with positional correlations of hexagonal in plane packing of molecules as well as layers tacking.

**Thermodynamic Parameters:**

By using dilatometer and specially designed pyknometer the temperature variation of density of liquid crystalline mixtures C1 and C2 is measured, which are illustrated in Figs. 6- 7. The density is found to decrease with increase of temperature. The density jumps are observed at phase transformations. The various thermodynamic parameters are estimated by using density and thermal expansion coefficient data.

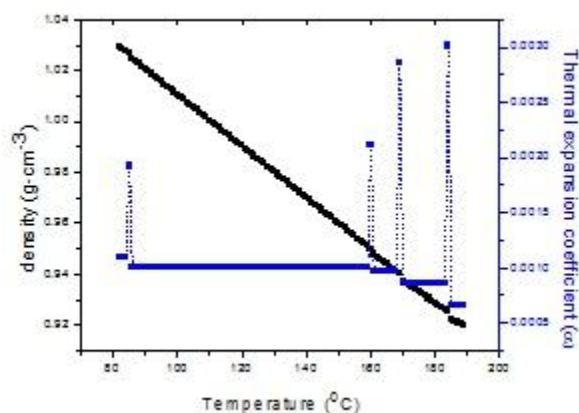


Fig. 6 Temperature variation of density of LC Mixture C1

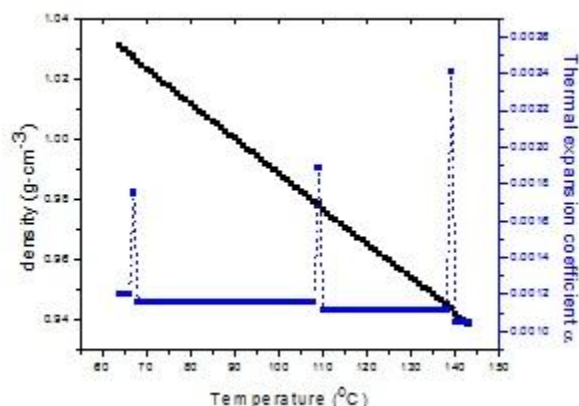


Fig. 7 Temperature variation of density of LC Mixture C2

**Table .5 Thermodynamic Parameters of C1 mixture**

T(K)	$\alpha$	C <sub>1</sub>	V~	X	So	F	$\Gamma$	f	A*
432	0.00101	7.2022	1.3355	-0.4660	1.1056	0.8842	5.5960	0.1457	1.0248
433(S <sub>A</sub> -S <sub>B</sub> )	0.00211	6.6396	1.5574	-0.2984	0.9929	0.0802	3.7475	0.1737	1.0365
434	9.70E-04	7.2653	1.3264	-0.4729	1.1077	0.9116	5.7388	0.1439	1.0241
441	9.70E-04	7.2366	1.3305	-0.4698	1.1068	0.8995	5.6742	0.1447	1.0244
442(N-S <sub>A</sub> )	0.00285	6.7992	1.6674	-0.2176	0.8746	-0.4619	3.4502	0.1782	1.0386
443	8.50E-04	7.4865	1.2992	-0.4939	1.1129	0.9918	6.2237	0.1380	1.0221
456	8.50E-04	7.4254	1.3061	-0.4886	1.1117	0.9718	6.0920	0.1395	1.0226

457(I-N)	0.00301	6.8864	1.6980	-0.1957	0.8322	-0.638	3.4119	0.1784	1.0387
458	6.50E-04	8.0850	1.2473	-0.5342	1.1193	1.1372	7.4676	0.1248	1.0178

Table .5 contd..

T(K)	B/A	$\Gamma_p$	$\beta\sim$	$\Gamma_{ih}$	$\Gamma_{ich}$	$\Gamma_{iba}$	$\Theta$	$\delta$
432	6.202201	3.4368	0.1244	3.1011	1.5838	1.5172	4.1676	3.0345
433(S <sub>A</sub> -S <sub>B</sub> )	5.639663	3.1563	0.0527	2.8198	1.2861	1.5336	3.5723	3.0673
434	6.265313	3.4683	0.1283	3.1326	1.6047	1.5279	4.2094	3.0559
441	6.236639	3.4540	0.1266	3.1183	1.5950	1.5232	4.1901	3.0464
442(N-S <sub>A</sub> )	5.799241	3.2367	0.0309	2.8996	1.2141	1.6854	3.4282	3.3709
443	6.486501	3.5788	0.1408	3.2432	1.6747	1.5685	4.3494	3.1370
456	6.425487	3.5483	0.1376	3.2127	1.6554	1.5573	4.3108	3.1146
457(I-N)	5.886479	3.2805	0.0260	2.9432	1.1983	1.7448	3.3967	3.4897
458	7.085027	3.8780	0.1674	3.5425	1.8508	1.6916	4.7017	3.3832

Table .6 Thermodynamic parameters of C2 mixture

T(K)	$\alpha$	C1	V~	X	So	F	$\Gamma$	f	A*
339	0.0012	7.3292	1.3179	-0.4795	1.1094	0.93715	5.8812	0.1453	1.0235
340(Cr.)	0.00175	6.8020	1.4213	-0.4006	1.0778	0.60734	4.5877	0.1789	1.0305
380	0.00116	7.1848	1.3382	-0.464	1.1050	0.87626	5.5564	0.1525	1.0250
381	0.00116	7.1804	1.3388	-0.4634	1.1048	0.87419	5.5462	0.1527	1.0251
382(S <sub>A</sub> )	0.00189	6.6753	1.4806	-0.3559	1.0479	0.39331	4.1387	0.1945	1.0335
398	0.00111	7.1811	1.3387	-0.4635	1.1049	0.87452	5.5478	0.1527	1.0250
399	0.00111	7.1769	1.3394	-0.4630	1.1047	0.87254	5.5382	0.1529	1.0251
400	0.00111	7.1727	1.3400	-0.4625	1.1046	0.87056	5.5286	0.1531	1.0251
405	0.00111	7.1523	1.3432	-0.4601	1.1038	0.86069	5.4814	0.1542	1.0254
406	0.00111	7.1483	1.3439	-0.4596	1.1036	0.85872	5.4721	0.1545	1.0254
407	0.00111	7.1443	1.3445	-0.4591	1.1034	0.85675	5.4629	0.1547	1.0255
408	0.00111	7.1404	1.3452	-0.4586	1.1033	0.85478	5.4537	0.1549	1.0255
409	0.00111	7.1364	1.3458	-0.4581	1.1031	0.85281	5.4445	0.1551	1.0256
410	0.00111	7.1326	1.3465	-0.4576	1.1030	0.85084	5.4355	0.1553	1.0256
411	0.00111	7.1287	1.3471	-0.4571	1.1028	0.84887	5.4264	0.1556	1.0257
412(IN)	0.00241	6.6577	1.5855	-0.2775	0.9675	-0.04633	3.6457	0.2152	1.0373
413	0.00105	7.2127	1.3340	-0.4672	1.1060	0.88901	5.6201	0.1510	1.0247

414	0.00105	7.2085	1.3346	-0.4667	1.1059	0.88714	5.6106	0.1512	1.0247
415	0.00105	7.2044	1.3352	-0.4662	1.1057	0.88526	5.6011	0.1514	1.0248
416	0.00105	7.2003	1.3358	-0.4658	1.1056	0.88339	5.5917	0.1517	1.0248

Table .6 contd..

T(K)	B/A	$\Gamma_p$	$\beta\sim$	$\Gamma_{ih}$	$\Gamma_{ich}$	$\Gamma_{iba}$	$\Theta$	$\delta$
339	6.3292	3.5003	0.1322	3.1646	1.6285	1.5360	4.2571	3.0721
340(Cr.)	5.8020	3.2370	0.0914	2.9010	1.4341	1.4668	3.8682	2.9337
380	6.1848	3.4281	0.1232	3.0924	1.5795	1.5129	4.1590	3.0258
381	6.1804	3.4259	0.1230	3.0902	1.5779	1.5122	4.1559	3.0244
382(S <sub>A</sub> )	5.6753	3.1738	0.0728	2.8376	1.3591	1.4784	3.7183	2.9569
398	6.1811	3.4263	0.1230	3.0905	1.5776	1.5128	4.1553	3.0257
399	6.1769	3.4242	0.1227	3.0884	1.5762	1.5122	4.1524	3.0244
400	6.1727	3.4221	0.1225	3.0863	1.5747	1.5115	4.1495	3.0231
405	6.1523	3.4119	0.1211	3.0761	1.5676	1.5084	4.1353	3.0169
406	6.1483	3.4099	0.1208	3.0741	1.5662	1.5078	4.1325	3.0157
407	6.1443	3.4079	0.1205	3.0721	1.5648	1.5072	4.1297	3.0145
408	6.1404	3.4059	0.1203	3.0702	1.5635	1.5067	4.1270	3.0134
409	6.1364	3.4040	0.1200	3.0682	1.5621	1.5061	4.1242	3.0122
410	6.1326	3.4020	0.1197	3.0663	1.5607	1.5055	4.1214	3.0111
411	6.1287	3.4001	0.1195	3.0643	1.5593	1.5049	4.1187	3.0099
412(IN)	5.6577	3.1655	0.0464	2.8288	1.2656	1.5632	3.5313	3.1264
413	6.2127	3.4421	0.1251	3.1063	1.5878	1.5185	4.1757	3.0370
414	6.2085	3.4400	0.1248	3.1042	1.5864	1.5178	4.1729	3.0356
415	6.2044	3.4379	0.1245	3.1022	1.5850	1.5171	4.1700	3.0343
416	6.2003	3.4358	0.1243	3.1001	1.5836	1.5165	4.1672	3.0330

The Moelwyn-Huges parameter C1 decreases with increase of temperature and exhibiting a very low value at liquid crystalline phase transition. The Moelwyn-Huges parameter value is 6.8864, 6.7992 and 6.6396 at I-N, N-SmA and SmB transitions in C1 and 6.6577, 6.67 I-N, N-SmA transitions in C2. This are illustared in Fig.8.

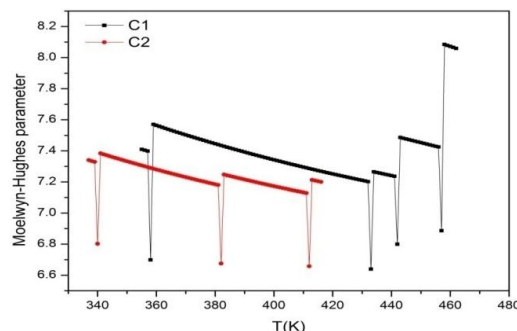


Fig.8. The Variation of Moelwyn-Hughes parameter with temperature in C1 and C2

The reduced Molar volume ( $\tilde{V}$ ), increases with increase of temperature and at phase transition there is a sudden hike in this value. At phase transition the values of this parameter are 1.6980, 1.6674 and 1.5574 at I-N, N-SmA and SmB transitions in C1 and 1.5855, 1.4806 at I-N, N-SmA a transitions in C2. The reduced Bulk modulus decreases with increase of temperature and in phase transformation there is drastic decrease in this value i.e., 0.026, 0.039 and 0.0527 at different phases in C1 and 0.0464, 0.0728 in C2. These are represented in Fig. 9.

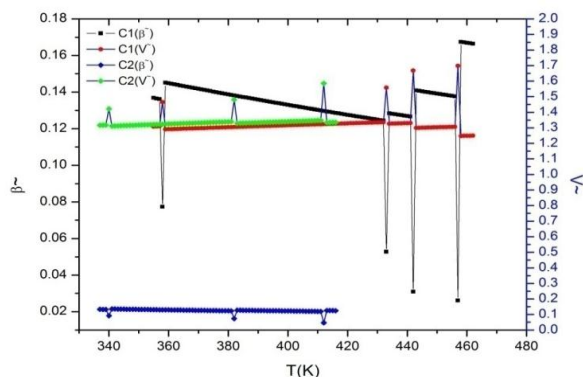


Fig.9 The variation of reduced bulk modulus and reduced molar volume with temperature in C1 and C2

The Bayer's non linearity and fractional free volume parameters decreases at different liquid crystalline phase transitions which are shown in Fig. 10. The fractional free volume ( $f$ ) increases at different liquid crystalline phases represented in Fig. 11.

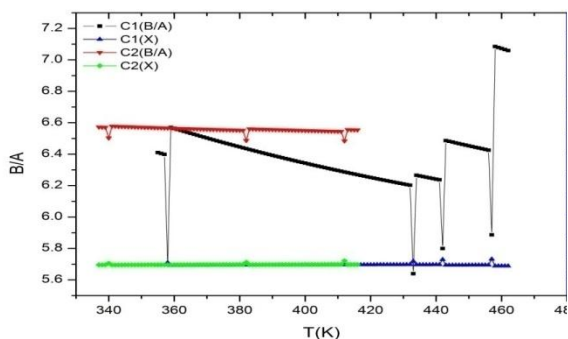


Fig.10 The variation of B/A and X with temperature in C1 and C2

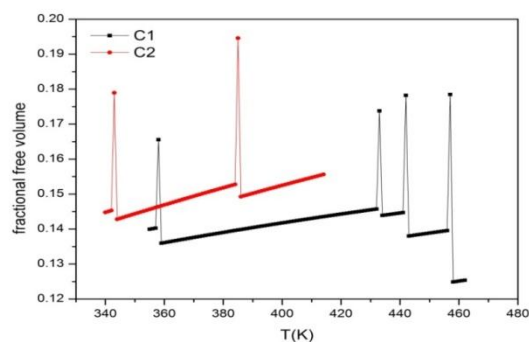


Fig 11. The variation of fractional free volume with temperature in C1 and C2

## V. CONCLUSION

The slopes of the density in nematic, smectic A and smectic B phases are found to be higher suggesting the closer packing of molecules than in isotropic phase. From these studies it is also observed that the sudden change in density and sharp discontinuity in thermal expansion coefficient attributes to the sudden change from order LC phases to disorder isotropic phase. As this phases differ mainly in the degree of molecular orientations. Due to this thermodynamic parameters also differ at phase transitions.

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