International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2025: 7.089

Assessment of Thermodynamic and Bayer's Nonlinearity Parameter in Two Different Series of Liquid Crystals-Dilatometric Study

Rihana Banu

Department of Physics, Govt. First Grade College, Yelahanka Bangalore-560064 Karnataka, India
Corresponding Author Email: *rihanabanu786[at]gmail.com*

Abstract: ***In the present work density measurements are carried out on 1. P-Cyanobenzylidene P Nonyloxyaniline and 2. P - Decyloxybenzylidene P-Toluidine liquid crystalline compounds. The density is found to decrease with increase of temperature in liquid crystalline phases expect in the vicity of phase transition it shows steep increase before it attains equilibrium value of the next phase. Using density data the various thermodynamic parameters like Moelwin Hughes parameter, Isochoric temperature coefficient of internal pressure, Huggin's parameter, Gruneisen parameter, Sharma parameter etc. are evaluated. The Bayer's nonlinearity parameter is also estimated. All the parameters show discontinuity at phase transformation (either dip or elevation). The results are discussed with reference to the literature data available on number of compounds. Key words: Liquid crystals, density, phase transition, thermodynamic parameters, Bayer's nonlinearity parameter.***

Keywords: Liquid crystals, phase transition, thermodynamic parameters, Bayer's nonlinearity parameter

1. Introduction

The liquid crystal materials exhibit a variety of mesophases with change of rigid core, side chain and terminal groups [1-4]. The lengthy terminal side chains quench the high temperature nematic phase thereby manifesting the smectic phases. The position of oxygen atom in the molecular moiety changes the transition temperatures. Further the dilatometric studies involving temperature variation across different phase transformation in liquid crystal materials provide information regarding the nature of phase transition and pre transitional effects [5-9]. The compounds viz., P-Cyanobenzylidene P-Nonyloxyaniline and P-Decyloxybenzylidene P Toluidine differs from other compounds with electro negative oxygen atom on right side of therigid core in first compound and on the left side of the rigid core in the second compound. Both the compounds shows Nematic and Smectic phases however the clearing temperature of the first compound is more than second compound. In the present work the density measurements as a function of temperature are carried out and the thermal expansion co-efficient at phase transition are noted. By using density and thermal expansion coefficient data the number of thermodynamic parameters are evaluated and results are discussed. The molecular formula of the liquid crystals used is shown below. C1: NCC6H4CH = NC6H4O (CH2)8CH3 (P-Cyanobenzylidene P-Nonyloxyaniline) C2: CH3 (CH2)9O C6H4CH = NC6H4CH3 (P-Decyloxybenzylidene P-Toluidine) DSC Thermograms and Transition temperature of compound P- Cyanobenzylidene P Nonyloxyaniline and P-Decyloxybenzylidene P-Toluidine are shown in Fig.1, Fig.2 and Table 1.

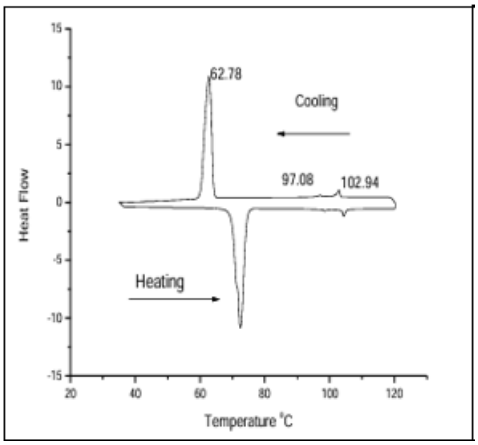

Figure 1: DSC Thermograms of compound P-Cyanobenzylidene P- Nonyloxyaniline

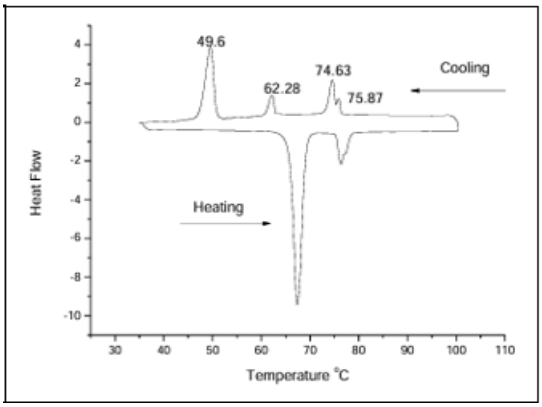

Figure 2: DSC Thermograms of compound P-Decyloxybenzylidene P- Toluidine

Table 1: Transition temperature in oC recorded by using Differential Scanning Calorimetry (DSC)

Compound	Transition temperature in °C		
	I-N	N-SmA	SmA-Cr
C1	102.94	97.08	62.78
C2	74.63	62.28	49.6

2. Experimental

The density measurements are done by using specially designed pyknometer is used. The pyknometer consists of capillaries with a diameter of about 300μm and 5 - 8 cms length is mounted on 'U' shaped glass tube. The pyknometer is calibrated by measuring the molar volume of water at different temperatures. The above liquid crystalline sample is filled in pyknometer and its mass is measured by using chemical balance. The pyknometer is kept in heating block of dilatometer and the temperature of the heating block is raised 5oC above the clearing temperature. Then the sample is slowly cooled until the sample level reaches the marks in capillaries. The excess sample in the cups of the capillaries was removed by syringe. Conventional cathetometer was used to measure the liquid crystal level in the capillaries. The main scale and vernier scale is replaced with a digital scale. A CCD camera is attached to the telescope and the levels of the capillary were observed on a monitor with a high magnification. By this technique the temperature variation of density and hence thermal expansion coefficient was measured to estimate various thermo dynamical parameters.

Theory and expressions: The theory for the estimation of different thermodynamic parameters using the coefficient of thermal expansion (α) is reported by several authors (Ranga Reddy et al., 1999[10]; Fakruddin et al., 2010[11]). The Moelwyn- Hughes parameter (Moelwyn-Hughes, 1951[12]), Beyer's nonlinearity parameter and the reduced molar volume (V˜) are evaluated from the following expression.

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

$$\left(\frac{B}{A}\right) = C_1 - 1 \quad (2)$$

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

Using the coefficient of thermal expansion Haward and Parker (Haward and Parker, 1968[13]) obtained an expression for the isochoric temperature coefficient of internal pressure (X) as

$$X = \frac{-2\,(1 + 2T)}{V^{c_1}} \quad (4)$$

The Sharma parameter (So) (Sharma, 1983[14]; Reddy et al., 2007[15]) is given by the expression

$$S_0 = \frac{-x}{2}\,(3 + 4\alpha T) \quad (5)$$

The isothermal microscopic Gruneisen parameter (Γ) is a measure of volume dependence of the harmonicity of the normal mode frequency (ν) of a molecular vibration of a polymer and is related to F and So as

$$\Gamma = \left(\frac{2}{3}\right)\alpha T + \left(\frac{2 + F + 4\alpha T}{2\alpha T}\right) \quad (6)$$

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 (Γ) as

$$f = \left(\frac{V_\alpha}{V}\right) = \left(\frac{1}{\Gamma + 1}\right) \quad (7)$$

Where Va 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.

$$A^* = \left(\frac{1 + f^2}{1 - f}\right) = 1 + \left(\frac{f}{\Gamma}\right) \quad (8)$$

The Gruneisen parameter (ΓP) for liquid crystals can be found

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

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 Γich could be evaluated using the following equation

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

Where

$$E = -2\,[1 + (\alpha T)^{-1}]\left[2\alpha\,(\tilde{V})^{C_1 - 1}\right] \text{ and } F = -2\alpha \quad (12)$$

The Huggins parameter (F) of a liquid crystal is related to S0 by the equation

$$F = 2\left[1 + \left(\frac{S_0}{3 + 4\alpha T}\right)\right] - \left(3 + \frac{4\alpha T}{3}\right) \quad (13)$$

3. Results and Discussions:

The temperature variation of density (ρ) and thermal expansion coefficient (α) for the liquid crystalline compounds is measured and illustrated in Fig. 3 and Fig.4. The density is found to decrease with increase of temperature in LC phases but in the vicinity of phase transition there is a steep jump in density. The density data is used to estimate the number of thermodynamic parameter viz, Moelwyn - Hughes parameter (C1), reduced molar volume(V˜), Isochoric Temperature Co-efficient of Internal Pressure(X), Sharma parameter (So), fractional free volume (f), Thermal parameter(A*), Gruneisen parameter(ΓP), Huggin's parameter(F) isothermal microscopic Gruneisen parameter(Γ), isothermal Gruneisen parameter(Γith), isochoric Gruneisen parameter(Γich), isobaric Gruneisen parameter(Γiba) and Bayer's nonlinearity parameter(B/A) and shown in table 2 and table 3. From our studies it is reported that the reduced molar volume and fractional free volume is found to increase with increase of temperature and there is a sudden increase in this values at phase transition. This is due to the fact that at phase transition the molecules in a compound align in a particular direction hence critical volume decreases, due to this reduced molar volume and fractional free volume increases. The percentage of increase in reduced molar volume in isotropic to nematic phase is 41% and Smectic to nematic phase is 24% in P-Cyanobenzylidene P-Nonyloxyaniline. In P-Decyloxybenzylidene P-Toluidine these values are 26% and 6.1% at Nematic to Isotropic and Smectic to Nematic phases. The lesser percentage in P Decyloxybenzylidene P-Toluidine may be due to high molecular weight and low transition temperature. Similar results are observed in fractional free

volume also. The Moelwyn - Hughes parameter (C1) and Bayer's nonlinearity parameter (B/A) decreases with decreases of temperature at phase transitions. There is a steep decrease in these values because these two parameters depend on compressibility. At phase transition the molecules in a compound are aligned in a particular direction and hence compressibility decreases therefore C1 and B/A values decreases. During isotropic- nematic transition the decreases in this values are very high when compared to smectic-nematic transitions. This is due to the fact that at higher temperatures compressibility is low; in liquid crystal research isotropic-nematic transition temperature is more than smectic - nematic transition temperature. Similarly, the values of the parameters viz, Isochoric Temperature Co-efficient of Internal Pressure(X), Sharma parameter (So), Thermal parameter(A*), Gruneisen parameter(ΓP), Huggin's parameter(F) isothermal microscopic Gruneisen parameter(Γ), isothermal Gruneisen parameter(Γith), isochoric Gruneisen parameter(Γich), isobaric Gruneisen parameter(Γiba) decreases at phases transitions.

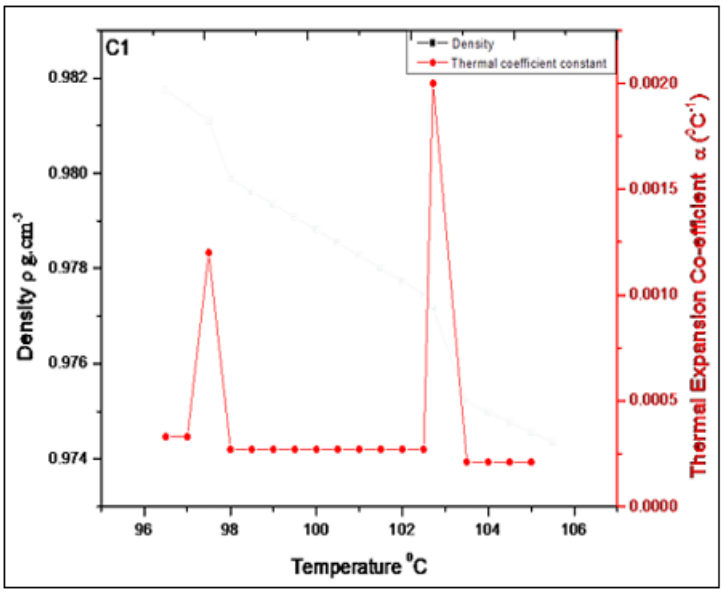

Figure 3: Temperature versus density and thermal expansion coefficient graph of compound P-Cyanobenzylidene P-Nonyloxyaniline

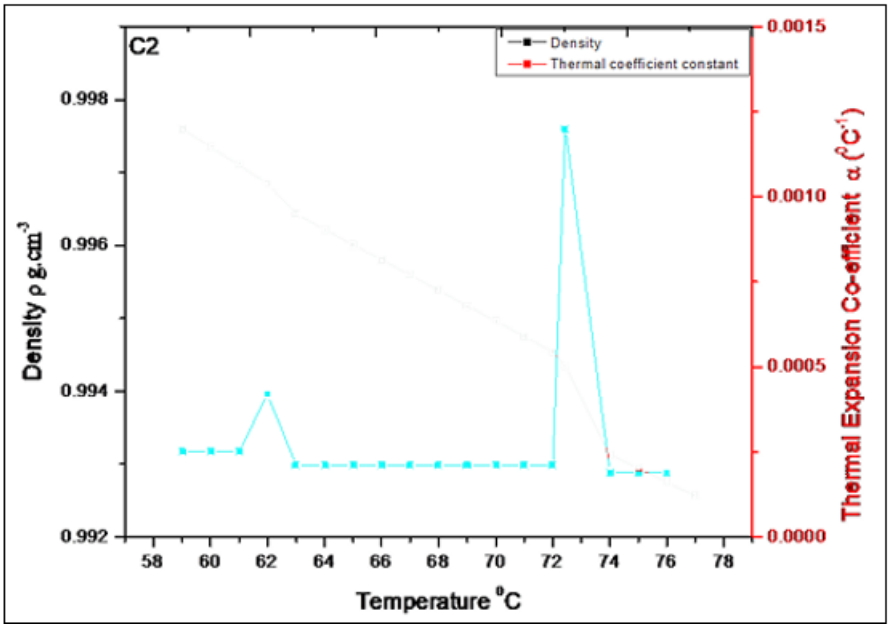

Figure 4: Temperature versus density and thermal expansion coefficient graph of compound P-Decyloxybenzylidene P-Toluidine

Table 2: Thermodynamic parameters of liquid crystalline compound (C1) P-Cyanobenzylidene P-Nonyloxyaniline

T(K)	α	C_1	$\tilde{V}$	X	S_o	f	A^*	Γ_p
369.5	0.00033	12.69326	1.112668	-0.64162	1.118897	0.074523	1.006001	6.181835
370	0.00033	12.6824	1.112808	-0.6415	1.118908	0.074593	1.006013	6.176404
370.5	0.0012	7.170531	1.34042	-0.4623	1.104525	0.146692	1.025218	3.421006
371	0.00027	14.44625	1.093841	-0.65704	1.117194	0.064816	1.004492	7.058294
371.5	0.00027	14.433	1.093959	-0.65694	1.117206	0.064879	1.004501	7.051666
372	0.00027	14.41978	1.094078	-0.65685	1.117218	0.064943	1.004511	7.045056
372.5	0.00027	14.40659	1.094196	-0.65675	1.117229	0.065007	1.00452	7.038464
373	0.00027	14.39344	1.094314	-0.65665	1.117241	0.065071	1.004529	7.03189
373.5	0.00027	14.38033	1.094433	-0.65655	1.117253	0.065134	1.004538	7.025334
374	0.00027	14.36725	1.094551	-0.65646	1.117265	0.065198	1.004547	7.018796
374.5	0.00027	14.35421	1.094669	-0.65636	1.117276	0.065261	1.004556	7.012275
375	0.00027	14.34121	1.094787	-0.65626	1.117288	0.065325	1.004566	7.005772
375.5	0.00031	13.07551	1.107934	-0.64548	1.118503	0.072162	1.005612	6.372951
376	0.00196	6.667083	1.487115	-0.35106	1.044021	0.167921	1.033888	3.16977
376.5	0.00021	17.08298	1.075076	-0.67253	1.115146	0.054236	1.00311	8.376621
377	0.00021	17.06634	1.075171	-0.67245	1.115157	0.054291	1.003117	8.368304
377.5	0.00021	17.04975	1.075265	-0.67238	1.115169	0.054347	1.003123	8.360009
378	0.00021	17.03321	1.07536	-0.6723	1.11518	0.054403	1.00313	8.351736
378.5	0.00021	17.01671	1.075454	-0.67222	1.115191	0.054459	1.003137	8.343485

Table 2(continued)

T(K)	F	Γ	Γ_{ith}	Γ_{ich}	Γ_{iba}	B/A
369.5	1.479037	12.41861	5.846632	3.072015	2.774617	11.69326
370	1.478702	12.40612	5.841201	3.069195	2.772005	11.6824
370.5	0.869499	5.816981	3.085265	1.574987	1.510278	6.170531
371	1.523481	14.42836	6.723127	3.520581	3.202546	13.44625
371.5	1.523204	14.41319	6.716499	3.517164	3.199335	13.433
372	1.522927	14.39807	6.709889	3.513757	3.196132	13.41978
372.5	1.522649	14.38299	6.703297	3.510358	3.192938	13.40659
373	1.522372	14.36794	6.696722	3.506969	3.189753	13.39344
373.5	1.522095	14.35294	6.690166	3.503589	3.186577	13.38033
374	1.521818	14.33798	6.683627	3.500218	3.183409	13.36725
374.5	1.52154	14.32306	6.677106	3.496856	3.18025	13.35421
375	1.521263	14.30818	6.670603	3.493504	3.177099	13.34121
375.5	1.490278	12.85773	6.037757	3.169746	2.868012	12.07551
376	0.368445	4.955182	2.833541	1.352442	1.481099	5.667083
376.5	1.567112	17.43807	8.041489	4.191147	3.850342	16.08298
377	1.566894	17.41912	8.033172	4.186884	3.846287	16.06634
377.5	1.566676	17.40021	8.024877	4.182633	3.842243	16.04975
378	1.566457	17.38136	8.016604	4.178393	3.83821	16.03321
378.5	1.566239	17.36255	8.008353	4.174165	3.834188	16.01671

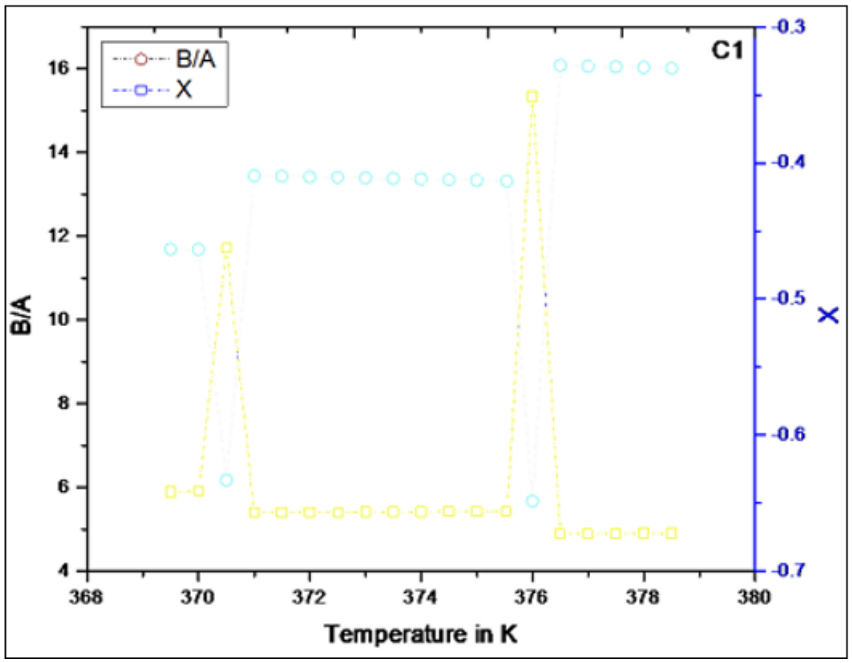

Figure 5: The variation of Beyer's parameter of nonlinearity (B/A) Isochoric Temperature Co-efficient of Internal Pressure (X) with temperature in P-Cyanobenzylidene P-Nonyloxyaniline compound

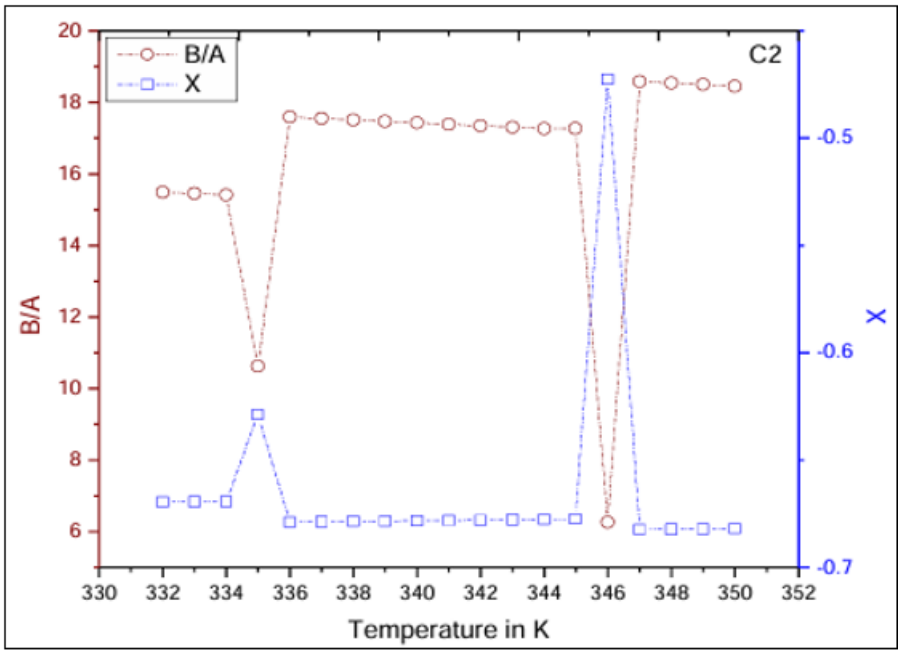

Figure 6: The variation of Beyer's parameter of nonlinearity (B/A) Isochoric Temperature Co-efficient of Internal Pressure (X) with temperature in P-Decyloxybenzylidene P-Toluidine compound

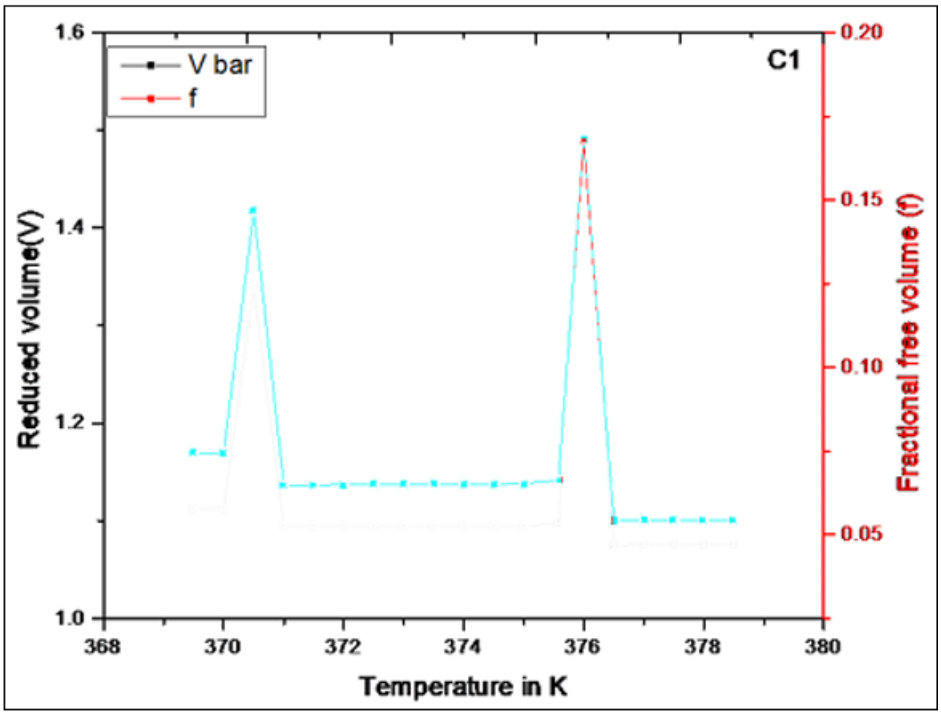

Figure 7: The variation of reduced volume (V˜), Fractional free volume (f) with temperature in P-Cyanobenzylidene P-Nonyloxyaniline compound

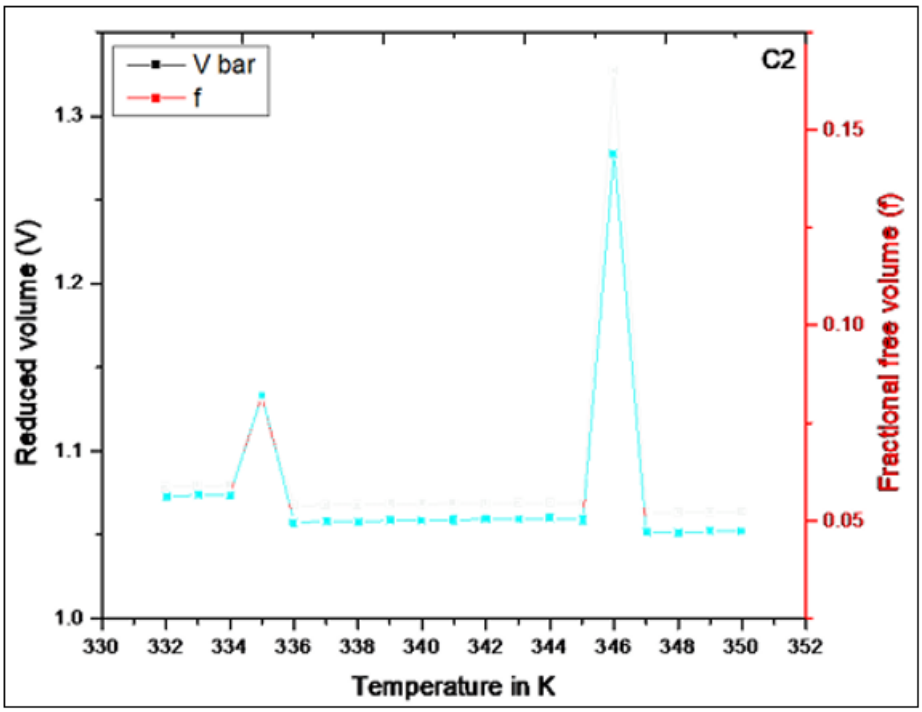

Figure 8: The variation of reduced volume (V˜), Fractional free volume (f) with temperature in P-Decyloxybenzylidene P-Toluidine compound Volume IX, Issue V, MAY/2019

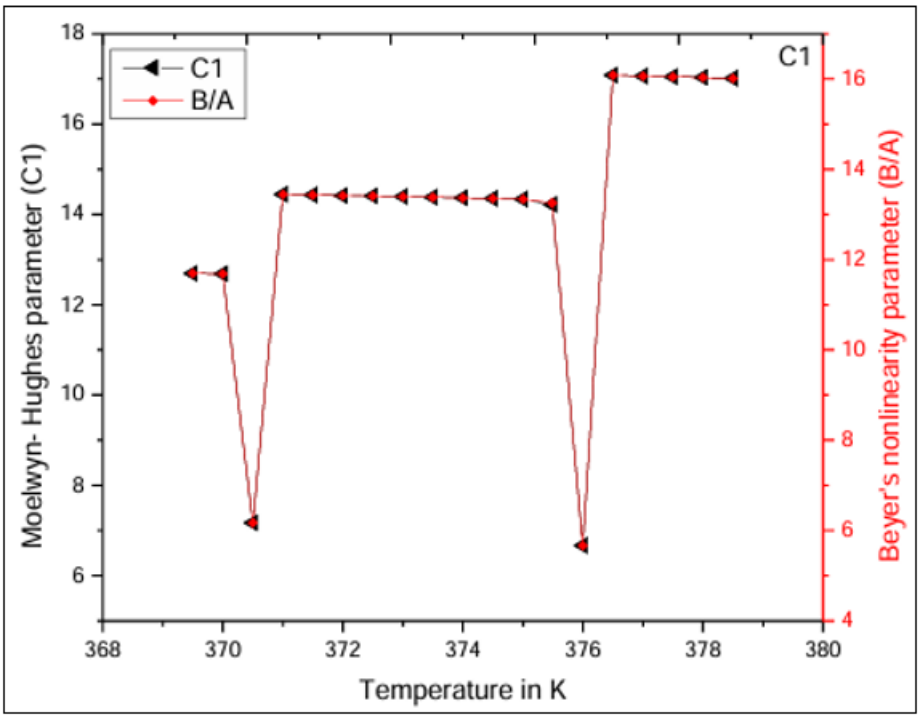

Figure 9: The variation of Moelwyn- Hughes parameter (C1), Beyer's nonlinearity parameter (B/A) with temperature in P-Cyanobenzylidene P-Nonyloxyaniline compound

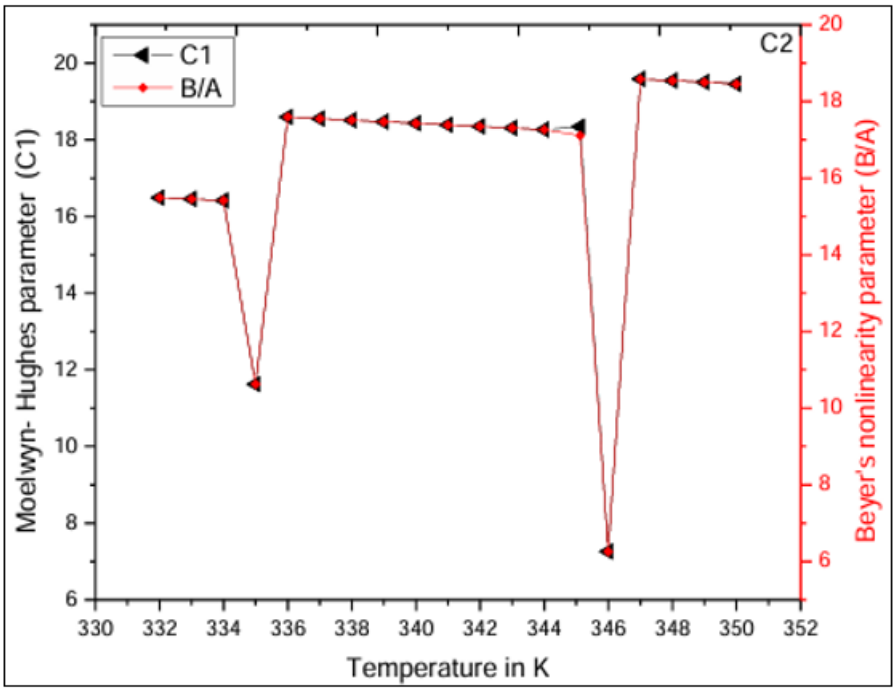

Figure 10: The variation of Moelwyn- Hughes parameter (C1), Beyer's nonlinearity parameter (B/A) with temperature in P-Decyloxybenzylidene P-Toluidine compound

4. Conclusion

From these studies it is noted that the sudden change in density and discontinuity in thermal expansion co-efficient attributes to the sudden change from ordered liquid crystal phases to disordered isotropic phase. These phases differs mainly in the degree molecular orientation due to this the thermodynamic parameters also changes at phase transitions.

References

[1] D J. Byron, D A Klating, M TO Neill, R CWillson, J W Goodby and G W Gray, Mol.Cryst. Liq. Cryst. Vol. 58(1980 pp 179)
[2] J Benatter, J Levelet and C Atrzelecki, J.Phys.(Paris) Vol. 39 (1978 pp 1233)'
[3] K. Fakruddin, R Jeevan Kumar, V. G.K.M. Pisipati, D. Madavi latha, B.T.P. Madhav and P.V. Datta Prasad, Mol.Cryst.Liq.Cryst. Vol. 524 pp. 102-118, 2010

[4] V. G. K.M. Pisipati, Z. Naturforsch Vol. 58a (2003 pp - 661)
[5] Gogoi B, Alapati P R and Verma A L, 2002, Cryst. Res. Tech. 37, 1331.
[6] Datta Pasad P.V, Ramakrishna Nanchara Rao M, Lalithakumari J and Pisipati V.G.K.M., 2009, phys.chem.liq.47,123.
[7] Burmistrov V A, Zavialoy A V, Novikoy I V, Kuvshinova S A and Aleksandriskii V. V., 2005(Russ. J. Phys. Chem., 79, 130).
[8] Ajeetha N, Rama Krishna Nanchara Rao M., Datta Prasad P V and V.G.K.M. Pisipati (2006), Mol. Cryst. Liq. Cryst. 457,3.
[9] Gogoi B, Gosh T K and Alapati P R (2005). Cryst. Res. Tech. 40,709.
[10] Ranga Reddy, R.N.V., Suryanarayana, A. and Rama Murthy V. 1999. Coefficient of volume expansion and Thermoacoustic Parameters of Alkyl-Cyano-Biphenyl Liquid Crystals. Cryst. Res. Technol. 34: 1299-1307.
[11] Fakruddin, K., Jeevan Kumar, R., Pisipati V.G.K.M., Madhavi Latha, D., Madhav, B.T.P. and Datta Prasad P.V. 2010. Phase Transitions and Thermodynamic parameters of N-(p n-octyloxybenzylidene)-p-n-alkoxyanilines-A Dilatometeric Study. Mol. Cryst. Liq. Cryst. 524: 102-118.
[12] Moelwyn-Hughes, E.A. 1951. The Determination of Intermolecular Energy Constants from common Physicochemical properties of Liquids. J. Phys. Chem. 55:1246-1254.
[13] Haward, R.N. and Parker, B.N. 1968. The internal pressure of simple liquids. J. Phys. Chem. 72:1842-1844
[14] Sharma, B.K. 1983. Nonlinearity parameter and its relationship with thermo-acoustic parameters of polymers. J. Phys. D: Appl. Phys. 16:1959.
[15] Reddy, R.R., Venkatesulu, A., Rama Gopal, K. and Neelakanteswara Reddy, K. 2007. Thermo acoustic parameters in the nematic and isotropic phases of 5CB and tetramethyl methane in 5CB. J. Mol. Liq. 130:112-118.