International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 5, Number 3 (2009), pp. 203–213

http://www.ripublication.com/ijpap.htm

Thermo-acoustic Studies of Trans-4-cyano Cinnamic Acid Ester Liquid Crystal

D.P. Singh and Arun Upmanyu*

Department of Physics, Govt. College, Dera Bassi-140507,
Dist. Patiala, Punjab, India
E-mail: drdpsn@hotmail.com
**Department of Physics, Patiala Institute of Engineering and Technology,*
Sirhind Road, Patiala-147001, Punjab, India
E-mail: arunupmanyu@gmail.com

Abstract

Intermolecular interaction studies of Trans- 4- cyano cinnamic acid ester have been done over the temperature range 340 K to 393 K, using ultrasonic velocity and density data taken from literature[1]. Several acoustical parameters such as adiabatic compressibility, isothermal compressibility, acoustic impedance, van der Waal's constants, molecular radius, space filling factor, surface tension, pseudo- Gruneisen parameter, Debye temperature, enthalpy and Poisson's ratio have been determined. Various thermo-dynamical parameters such as available volume, refractive index, molar refraction, Eykmann constant, internal pressure, intermolecular free length and relative association have also studied. Free Length Theory and Collision Factor Theory have been applied to predict the ultrasonic velocity values in the system. The obtained results has been explained in terms of the temperature dependence of theses parameter and the intermolecular interaction present in the system, The present investigation provide a rich source of information about the type and extent of molecular interaction occurring in the liquid crystal.

Introduction

Liquid crystals are substances that exhibit properties between those of a conventional liquid and a solid crystal. For instance, a liquid crystal (LC) may flow like a liquid, but have the molecules in the liquid arranged and/or oriented in a crystal-like way. There are many different types of LC phases, which can be distinguished based on their different optical properties (such as birefringence). When viewed under a microscope using a polarized light source, different liquid crystal phases will appear

to have a distinct texture. The each contrasting areas in the texture correspond to a domain where the LC molecules are oriented in a different direction. Within a domain, however, the molecules are well ordered. In addition to being in a liquid phase, LC materials may also be found in the solid and gaseous phase.

Liquid crystals can be divided into thermotropic and lyotropic LCs. A thermotropic LC exhibit a phase transition as temperature of the LC is changed, whereas a lyotropic LC exhibit phase transitions as a function of concentration of the mesogen in a solvent (typically water) as well as temperature.[2-9] The various LC phases (called *mesophases*) can be characterized by the type of ordering that is present. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientational order (whether molecules are mostly pointing in the same direction), and moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). Most thermotropic LCs will have an isotropic phase at high temperature. That is, heating will eventually drive them into a conventional liquid phase characterized by random and isotropic molecular ordering (little to no long-range order), and fluid-like flow behavior. Under other conditions (for instance, lower temperature), an LC might inhabit one or more phases with significant anisotropic orientational structure and short-range orientational order while still having an ability to flow.

The ordering of liquid crystalline phases is extensive on the molecular scale. This order extends up to the entire domain size, which may be on the order of micrometres, but usually does not extend to the macroscopic scale as often occurs in classical crystalline solids. However, some techniques (such as the use of boundaries or an applied electric field) can be used to enforce a single ordered domain in a macroscopic liquid crystal sample. The ordering in a liquid crystal might extend along only one dimension, with the material being essentially disordered in the other two directions.

Due to their ability to change colour in an electric field or with variation in temperature, the liquid crystals have wide range of applications. The resonance, electron paramagnetic resonance and differential scanning colourimetery enabled scientists to study more effectively the physical properties of liquid crystals. Their unusual physical and optical properties have important technological and commercial application. They are already being used in digital watches, digital readout memory systems and display devices.

It has been recently discovered that certain LCs such as R-C_6H_5-CH=CH-CO_2-C_6H_4-CN, exhibit a large positive anisotropy and dielectric constant, individually or in the form of mixture with other nematic or non-nematic substances. They also exhibit light viscosity at relativity low temperature. The advantage of these compounds is a substantially greater stability so that they can be handled more conveniently. The anomalous temperature behaviour of ultrasonic velocity in 8 OCB liquid crystal was studied by Srinivasa Manja[10] and phase transition study in Schiff's base ester liquid crystal carried out by Narasimhamurthy et al[5]. Using experimental ultrasound velocity and density data, as available in literature[1], an attempt is made to understand the nature, type and strength of molecular interactions prevalent in Trans-4-cyano

cinnamic acid ester over the temperature range 340 K to 393 K. Several prevalent theories of liquid and solid state of matter have been investigated. A qualitative as well as quantitative measure of the molecular interactions prevalent in the LC has been obtained in present investigation.

Theory

Several researchers[1-12] have reported that the thermo-acoustic parameters are a versatile tool to investigate molecular interactions in liquids or solids. Using theoretical formulae available in literature [10-25] a large number of acoustical and thermo-dynamical parameters such as molar volume (V), adiabatic compressibility (K_s), isothermal compressibility (K_T), Specific acoustic impedance (Z), Rao's constant (R), van der Waal's constants (a & b), available volume (V_a), Intermolecular free length (L_F), Relative association (R.A.), free Volume (V_f), internal pressure (p_i), molar cohesive energy (ΔH), Surface Tension (σ), Coefficient of viscosity (η), relaxation time (τ), Space filling factor (r_F), collision factor (S), molecular radius (r_m), Geometrical volume (B), refractive index (n_D), Eykmann constant (E_C), Molecular refraction (M_R), Coefficient of thermal expansion (α), Specific heat ratio (γ), Poisson's ratio ($_0$-), Young modulus (E), Bulk modulus (B), Shear modulus (G), Latent heat of melting (ΔH_m), Diffusion constant (D_i), molecular diameter (d_o), Coefficient of thermal conductivity (k), Debye temperature (θ_D) and Pseudo Gruneisen parameter (Ґ). Ultrasonic velocity values have been determined in the system under investigation using Free Length Theory (FLT) [15] and Collision Factor Theory (CFT)[24]. Some of the important formulae are listed below.

Adiabatic compressibility = $K_S = \frac{1}{u^2 d}$, where d is the density of LC and u is the ultrasonic velocity in it. (1)

Isothermal compressibility= $K_T = \frac{1.71\times10^{-3}}{T^{4/9} u^2 d^{4/3}}$, where T is the temperature of the system. (2)

Specific acoustic impedance = $Z = ud$ (3)

van der Waal's pressure constant = $a = P_i V^2$, where V is the molar volume and P_i is the internal pressure of the LC. (4)

Co-Volume = $b = \left(\frac{M}{d}\right)\left[1 - \frac{RT}{Mu^2}\left\{\left(1 + \frac{Mu^2}{3RT}\right)^{1/2} - 1\right\}\right]$, where M is molar weight of the LC and R is Universal Gas Constant. (5)

Intermolecular free length = $L_f = \frac{2V_a}{Y_S}$, where $Y_S = (36\pi NB)^{1/3}$ is molar surface area, $V_a = V\left(1 - \frac{u}{u_\infty}\right)$ is the available volume, N= 6.0225×10^{23} mol^{-1}, $B = \frac{b}{S}$ is the Geometrical volume of the system and u_{00}= 1600 m/s. (6)

Relative association = $R.A. = \left[\frac{L_f}{L_f'}\right]^2$, where L_f' is the intermolecular free length found by using ultrasonic velocity values. (7)

Free Volume = $V_f = V - b$, where V is the molar volume of the LC. (8)

Internal Pressure = $P_i = \left[\frac{B'RT}{(V_f V^2)^{1/3}}\right]$, where $B' = 2$ (9)

Molar cohesive energy = $\Delta H = P_i V$ (10)

Surface Tension = $\sigma = 10^{-4} u^{3/4} dT^{1/3}$ (11)

Coefficient of viscosity = $\eta = \frac{Mu}{KV_f^{2/3}}$, where K is 4.28 x 10^8. (12)

Relaxation time = $\tau = \eta K_S$ (13)

Space Filling Factor = $r_F = \frac{B}{V}$ (14)

Collision Factor = $S = 4\left(1 - \frac{T}{ab^2}\right)$ (15)

Refractive index w.r.t. D-line of Sodium = $n_D = \sqrt{\frac{1+2r_F}{1-r_F}}$ (16)

Eykmann constant = $E_C = \left[\frac{n_D{}^2 - 1}{(n_D + 0.4)d}\right]$ (17)

Molecular refraction = $M_R = \left[\frac{n_D{}^2 - 1}{n_D{}^2 + 2}\right]V$ (18)

Coefficient of cubical thermal expansion = $\alpha = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/2} d^{1/3}}$ (19)

Specific heat ratio = $\gamma = \frac{K_T}{K_S}$ (20)

Molecular diameter = $d_o = 2r_m$, where molecular radius = $r_m = \left(\frac{3B}{4\pi N}\right)^{1/3}$ (21)

Poisson's Ration = $\sigma_{ps} = \left(\frac{3A-2}{6A+2}\right)$, where A = $\frac{4}{3\gamma}$ (22)

Young modulus = $E = u_l^2 d$ (23)

Shear modulus = $G = u_T{}^2\, d$ (24)

Bulk modulus = $K = \frac{3E-4G}{3}$ (25)

Latent heat of melting = $\Delta H_m = \frac{9M}{128}\left(\theta_D d_o \frac{k}{h}\right)^2$, where k is Boltzmann Constant and h is Planck's constant. (26)

Diffusion constant = $D_i = \frac{k d_o^2 \theta_D}{96h}$, (27)

Coefficient of thermal conductivity = $k = 2.8k\left(\frac{dN}{M}\right)^{2/3} \gamma^{-1/3} u$ (28)

Debye temperature = $\theta_D = \frac{h}{k}\left(\frac{3N}{4\pi V}\right)^{1/3} u$ (29)

Pseudo Gruneisen parameter = $\Gamma = \frac{\gamma - 1}{T\alpha}$ (30)

The results obtained for the LC by using the above given formulae, are presented in Tables 1to 3. Temperature dependence of some of the thermo-acoustic parameters is presented in Figs. 1 to 14. The values of all the parameters are reported in SI units.

Results

Table 1: Temperature dependence of some acoustical parameters of trans-4-cyano cinnamic acid ester.

Temp (K)	$\alpha \times 10^3$	φ/B	$R \times 10^6$	$E_C \times 10^6$	$M_R \times 10^6$
340	1.089	1.52	3300	5.229	72.62
346	1.097	1.51	3306	5.261	73.07
352	1.106	1.51	3316	5.297	73.57
358	1.116	1.50	3322	5.333	74.04
364	1.129	1.49	3324	5.368	74.57
370	1.143	1.48	3333	5.414	75.21
375	1.155	1.47	3345	5.461	75.88
379	1.118	1.45	3330	5.510	76.55
383	1.173	1.46	3391	5.620	77.38
387	1.181	1.46	3491	5.635	78.22
393	1.198	1.45	3425	5.677	78.89

Table 2: Temperature dependence of some acoustical parameters of trans-4-cyano cinnamic acid ester

Temp (K)	γ	$d_o \times 10^{12}$	$\eta \times 10^3$	u_l	u_T
340	1.2767	612.9	1.86	1279	1977
346	1.2691	614.1	1.80	1257	1942
352	1.2633	615.4	1.74	1239	1913
358	1.2570	616.9	1.67	1213	1877
364	1.2452	618.3	1.61	1188	1839
370	1.2461	620.1	1.54	1158	1795
375	1.2427	621.9	1.48	1135	1761
379	1.2080	623.8	1.40	1069	1670
383	1.2418	625.9	1.40	1110	1723
387	1.2377	627.8	1.37	1098	1705
393	1.2342	630.0	1.30	1071	1663

Table 3: Temperature dependence of some acoustical parameters of trans-4-cyano cinnamic acid ester.

Temp (K)	a	$r_m \times 10^{10}$	S	$P_i \times 10^4$	σ_{ps}
340	4.96	306.45	3.999	5452	0.1371
346	5.05	307.71	3.999	5469	0.1393
352	5.14	307.78	3.998	5486	0.1399
358	5.21	308.43	3.998	5483	0.1413
364	5.32	309.16	3.998	5500	0.1425
370	5.41	310.96	3.998	5487	0.1437
375	5.49	310.96	3.998	5468	0.1445
379	5.53	311.88	3.998	5390	0.1521
383	5.68	312.99	3.998	5421	0.1466
387	5.77	313.90	3.998	5407	0.1455
393	5.87	315.02	3.998	5374	0.1463

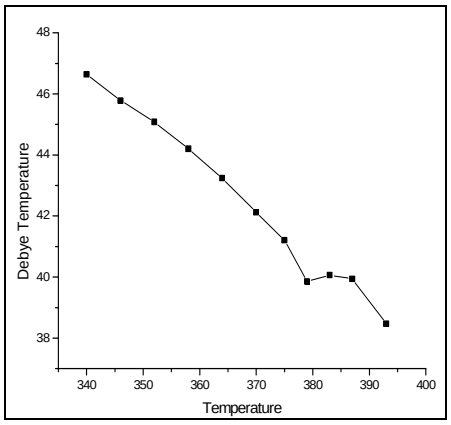

Figure 1: Variation of Debye Temperature with temperature.

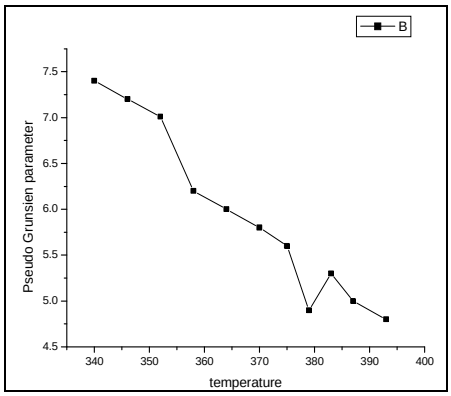

Figure 2: Variation of pseudo Grunsien parameter with temperature.

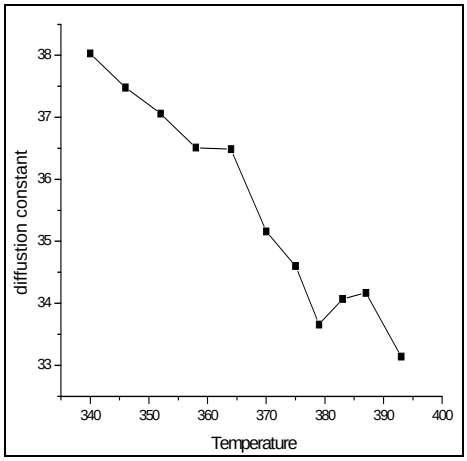

Figure 3: Variation of diffusion constant with temperature.

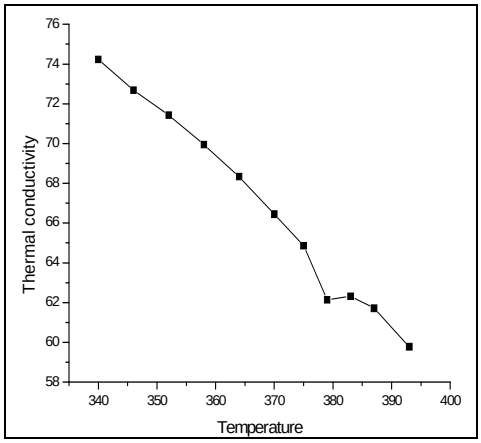

Figure 4: Variation of thermal conductivity with temperature.

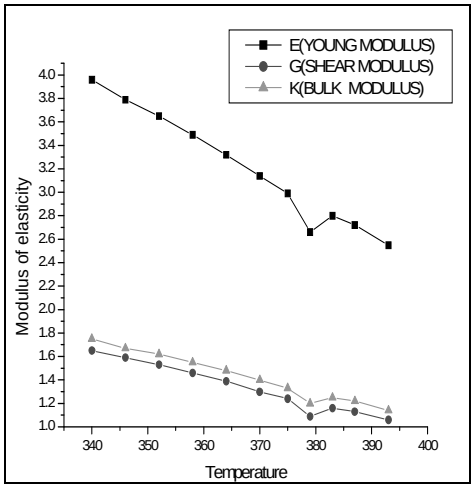

Figure 5: Variation of E, G and K with temperature.

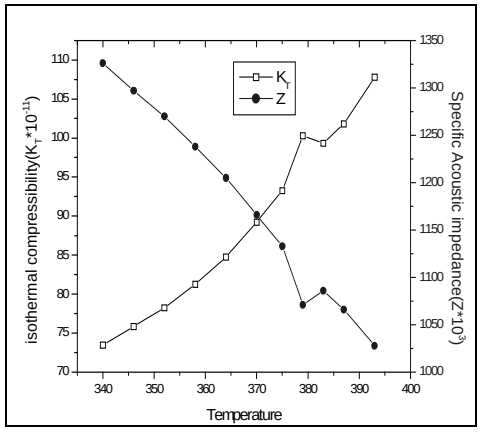

Figure 6: Variation of Z K_T with temperature.

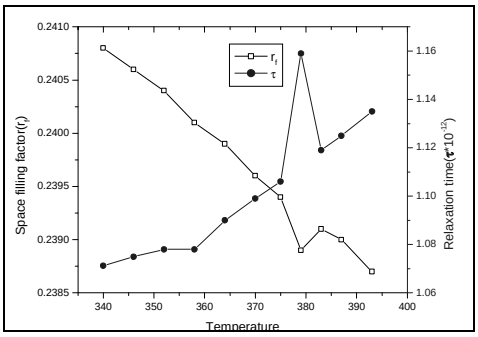

Figure 7: Variation of r_r and t with temperature.

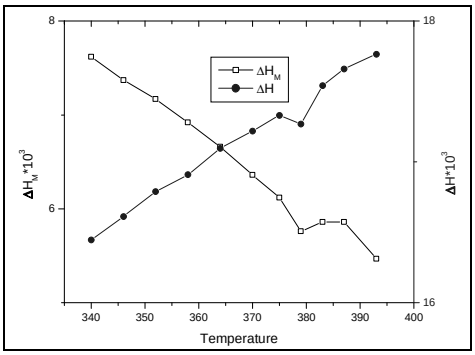

Figure 8: Variation ΔH_M and ΔH with temperature.

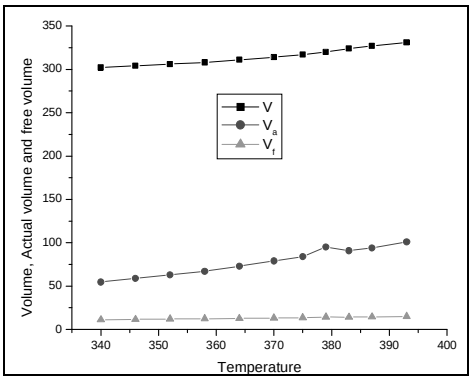

Figure 9: Variation of V, V_a and V_r with temperature.

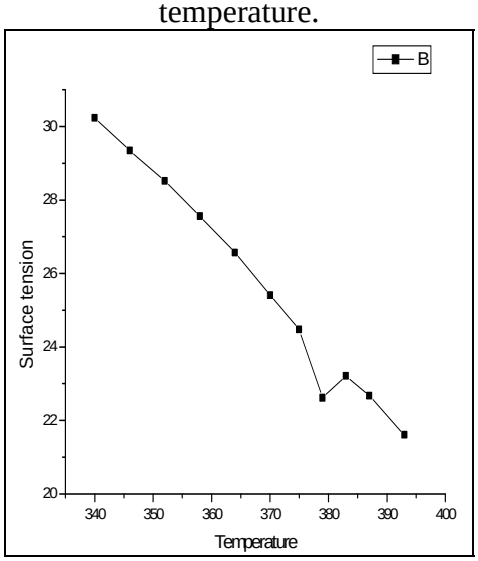

Figure 10: Variation of surface tension with temperature.

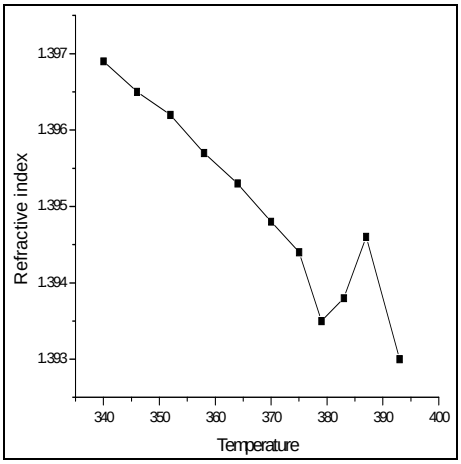

Figure 11: Variation of refractive index with temperature.

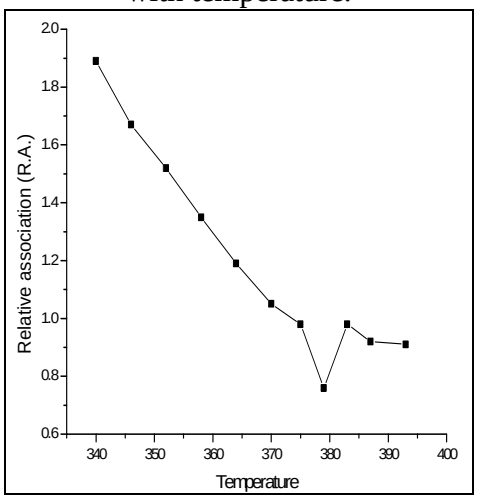

Figure 12: Variation of relative association (R.A) with temperature.

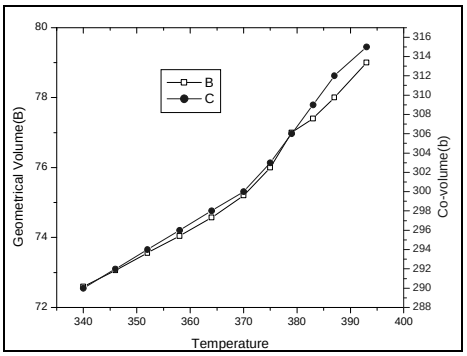

Figure 13: Variation of B and b with temperature.

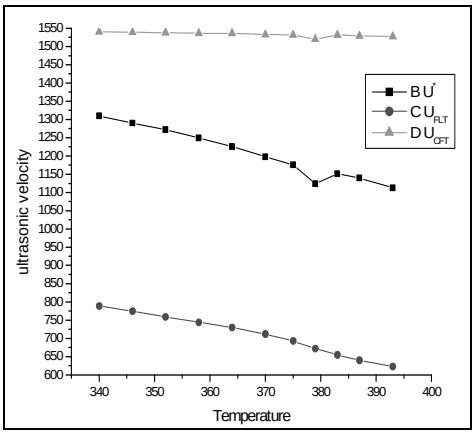

Figure 14: Variation of ultrasonic velocity with temperature.

Discussion and Conclusions

As low amplitude, low frequency ultrasonic waves don't deform structure of the medium through which they propagate. They merely perturb its physico-chemical equilibrium. The velocity of such waves is a thermodynamic quantity intimately connected with the residual equilibrium properties. The velocity of ultrasonic waves in a medium and several other acoustical parameters, which are dependent on it, help us to determine the overall response of the medium and tell us about the nature of interactions between the molecules of the medium[16-19].

For the system under study, the ultrasonic velocity (u) and density (d) data used to evaluate various acoustical and thermo-dynamical parameters has been taken from literature[1]. The temperature variation of some thermo-acoustic parameters of the trans-4-cyano cinnamic acid ester liquid crystal under investigation is presented in Tables 1 to 3. The temperature variation of some solid-state parameters such as Debye temperature (θ_D), Pseudo-Gruneisen parameter (Γ), Young's Modulus (E), Shear Modulus (G), Bulk Modulus (K), Diffusion Constant (D_i) and Thermal conductivity (k) are presented in Figs. 1-5 respectively.

The variations of several acoustical and thermo-dynamical parameters such as Specific acoustic impedance (Z) and Isothermal compressibility (K_T), Surface tension (σ), relative association (R.A.), co-volume (b), relaxation time (τ), Latent heat of vapourisation (ΔH), Latent heat of Melting (ΔH_m), molar volume (V), available volume (V_a), free volume (V_f), Geometric Volume (B), Space filling factor (r_f), and refractive index (n_D), with temperature from 340K to 393K are presented in Figs. 6-13 respectively. The temperature dependence of experimental ultrasonic velocity (U*) and the velocity values as computed from Collision Factor Theory (U_{CFT}) and Free Length Theory (U_{FLT}) are presented in Fig. 14.

A liquid can be treated either as a limiting case of a solid or as a highly condensed gas. Various parameters derivable from the ultrasonic velocity have been evaluated and their behaviour has been investigated with changing temperature. Some of these properties, such as Gruneisen parameter, Debye temperature, Poisson's ratio, elastic

modulii and Latent heat of melting come from considering the solid-like characteristics of the liquid crystal. Others, like free volume, isentropic compressibility, isothermal compressibility, diffusion constant, ratio of specific heats and co-volume are extensions of the concepts valid for gases[16].

The perusal of Figs. 1-4 show that the solid state parameters θ_D, Γ, $D_{i,}$ and k for the system under study gradually decreases with rise in temperature from 340K to 393K, and show a sharp dip near 379K indicating a crystalline structural change at the temperature. In Fig. 5, elastic modulii E, G and K show similar kind of behaviour to that observed in above said parameters. This trend of variation of elastic modulii of the LC further support the conclusion arrived at earlier.

The K_T (Fig. 6), τ (Fig. 7) and B (Fig. 13) show regular rise with increase in temperature from 340K to 393K. All these parameters show a peak at 379K. It may be due to the fact that in vicinity of phase transition a hetero-phase is expected which leads to vigorous fluctuations. The perusal of Figs 6-8 and 10-12, points to the variation of Z, r_f , ΔH_m, $\sigma_{,}$ $n_{D,}$ R.A. with rise in temperature respectively. All these parameters regularly decrease with rise in temperature from 340K to 393K with a dip at 379K.

A comparative study of the experimental ultrasonic velocity values in the system under investigation and theoretically evaluated ultrasonic velocities, using Collision Factor Theory (CFT) and Free Length Theory (FLT), is presented in Fig. 13. It can be seen that U*, U_{CFT} and U_{FLT} regularly decrease with rise in temperature from 340 K to 393 K. U_{FLT} decreases smoothly, without indicating any sudden change in the system whereas U_{CFT} and U* show a dip at 379 K, which is smaller in case of U_{CFT} vs T graph than in U* vs T graph. As is obvious from the Fig.13 CFT over-estimate whereas FLT under-estimates the values of ultrasonic velocity in the system. Hence both these theories fail to describe the behaviour of the Liquid crystal within the given temperature range, accurately. The perusal of Fig. 9 points out that V and V_a increase with rise in temperature and each of these parameters shows a peak at 379K. However free volume (V_f) remains almost constant within the temperature range under study.

A perusal of Table 1 indicate that R, $E_{C,}$ M_R and α regularly increase with rise in temperature from 340K to 393K, but R and α show a dip at 379K. The ratio of molar sound volume and Geometric volume show a slight decrease from 1.52 to 1.45 with rise in temperature. The results presented in Table 2 indicate that γ and η regularly decrease with rise in temperature but show a dip at 379K. In Table 3 calculated values of van der Waal's pressure constant (a), molecular radius ($r_{m)}$ and Poisson's ratio (σ_{ps}) are presented which show a regular increase with rise in temperature. The σ_{ps} values indicate a peak at 379K. In Table 3 the Collision Factor (S) and Internal Pressure (P_I) values are also presented. It may be noted that Pi values do not show any regular variation with temperature change whereas the collision factor (S) remains constant throughout. The general trend of the variations of the various acoustical and thermo-dynamical parameters agrees fairly well with the conclusions of the weakening of quasi crystalline structure in the system with rise in temperature in general.

These thermo-acoustic investigations of the trans-4-cyano cinnamic acid ester liquid crystal provide a qualitative as well as a quantitative measure of the strength of molecular interactions present in the system. It is further concluded that with the rise of

thermal agitations in the system there is a strong possibility of realignment / restructuring of the molecules in the liquid crystal especially at a temperature of 379K.

References

[1] Narasmhamurthy, Y., Ranga Reddy, R.N.V. and Murthy, V. R., J. Pure Appl. Ultrason. 23(2001)6-9

[2] de Gennes, P.G. and Prost, J., The Physics of Liquid Crystals, Oxford: Clarendon Press. (1993) ISBN 0-19-852024-7.Chandrasekhar, S., Liquid Crystals, (2nd Edition) Cambridge: Cambridge University Press. (1992) ISBN 0-521-41747-3.

[4] Sluckin, T. J., Dunmur, D.A., and Stegemeyer, H., Crystals That Flow, London: Taylor & Francis. (2004) ISBN 0-415-25789-1.Dierking, Textures of Liquid Crystals, Weinheim: Wiley-VCH. (2003) ISBN 3-527-30725-7.Kleinert, H. and Maki, K., Lattice Textures in Cholesteric Liquid Crystals, Fortschritte Physik **29**(1981)1.Collings, P.J. and Hird, M., Introduction to Liquid Crystals, Bristol, PA: Taylor & Francis. (1997) ISBN 0-7484-0643-3Martin, J.D., Keary, C.L., Thornton, T.A., Novotnak, M.P., Knutson, J.W. and Folmer, J.C.W., Nature Materials **5 (2006)** 271–275.Movahed, H.B., Hidalgo, R.C. and Sullivan, D.E., Phys. Rev. E (March 2006)73.

[10] Anbananthan, D., Krishnan, B., and Srinivasa Rao, A., Indian J. Chem., 13 (1975) 512., 14/4 (1976)277.

[11] Rajulu, A.V., Bhaskar, B. and Sumti, S.C., J. Pure Appl. Ultrason., 17(1995)107-109.

[12] Auerbach, R., Pannling, O. and Keit, S., Experimentia, 4 (1948) 473.

[13] Auerbach, N., Kolloidz, Experimentia, 113 (1949) 145.

[14] Birendra, B., and Chandra, S. J, Phys. C. (Solid State Phys.), 95(1976); Acustica 37, 277 (1975); Acustica, 33, 217 (1975).

[15] Jacobson, B., Acta. Chem. Scand. 6 (1952) 1485; J. Chem. Phys., 20 (1952) 927

[16] Bhatti, S.S and Singh, D.P., Ind J. Pure and App. Phys., 20, 961(1982).

[17] Patil, D.P. and Padmini, A. R.K.L., J. Acoust. Soc. India, 8 (1980) 5-11.

[18] Singh, D.P., J. Acoust. Soc. India, 14 (1986) 79-84.

[19] Bhatti, S.S., Virk, J. S., Lark, B.S. and Singh, D.P., J. Pure Appl. Ultrason., (1981)11-14.

[20] Colloquium on HTBP-ISRO-VSSC SP 64- 92 (1992).

[21] Bhatti, S.S. and Lark , B.S., Acustica, 48 (1981) 64.

[22] Devries, A., Mol. Cryst. Liq. Cryst. 21 (1973) 239.

[23] Dewan, R.K., Gupta C.M. and Mehta, S.K., Acustica, 65(1988) 245.

[24] Schaaffs, W. Acustica, 33(1975) 272.

[25] Dhanalakshmi, A., J. Acoust. Soc. India, 8/2 (1980) 29.