Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/13731
DOI URL: http://dx.doi.org/10.21474/IJAR01/13731

ISSN NO. 2320-5407

RESEARCH ARTICLE

PHASE TRANSITION STUDIES OF CHOLESTERYL PALMITATE, CHOLESTERYL DECANOATE AND THEIR MIXTURES USING DIELECTRIC, EPR AND DTA TECHNIQUES

Sanjai Misra
Department of Physics, B.S.N.V.P.G.College, Lucknow, 226001, U.P., India.

……

Manuscript Info

Manuscript History
Received: 11 September 2021
Final Accepted: 14 October 2021
Published: November 2021

Key words:-
Dielectric Constant, Order Parameter, Phase Transition, Liquid Crystal

Abstract

The phase transition of two liquid crystalline materials, namely cholesteryl palmitate and cholesteryl decanoate and their mixtures (by weight)are studied using dielectric, Electron paramagnetic resonance (EPR) and differential thermal analysis (DTA) techniques. From the dielectric measurements, the phase transition temperatures were determined from the discontinuities in the curve between dielectric constant and temperatures for all the samples investigated. Further, since mixing of two liquid crystals modifies the transition of phases, the measurements were carried out on the mixtures of the two liquid crystals. Order parameter for each sample was calculated at varying temperatures by measuring the hyperfine splitting of three line EPR spectrums. The discontinuities in the curve between order parameter and the temperature again indicated the phase transition of the liquid crystals and their mixtures. A DTA study on these samples was also carried out in order to probe further their transitional behaviour. The DTA records of both the liquid crystals and their mixtures support the transition behaviour observed from the dielectric and EPR measurements.

Copy Right, IJAR, 2021,. All rights reserved.

……

Introduction:-

The study of phase transition of liquid crystalline materials has been considered to be one of the very interesting subjects for both experimental and theoretical investigations. Liquid crystals are highly anisotropic fluids that exist between the boundaries of the solid phase and the conventional, isotropic liquid phase. The phase is a result of long range orientational ordering among constituent molecules that occurswithin a certain range of temperature in melts and solutions of many organic compounds. The ordering is sufficient to impart some solid-likeproperties to the fluid but the forces of attraction usually are not strongenough to prevent flow. The term liquid crystal thus refers to the phasethat lies between the rigidly ordered solid phase where the mobility ofindividual molecule is restricted and the isotropic phase where molecularmobility and a general lack of molecular order exist.As a result, there isanisotropy in the mechanical, electrical and optical properties. Thedielectric and optical studies of liquid crystal are important as theyprovide information about molecular structure, intermolecular forcesand moleculardynamics [HillN.E. et al (1969)]. Structural changes arising from the transitionbetween the mesophases of liquid crystalline materials are generally studied using optical properties [Brown G.H. et al (1971), Nagappaet al (1991), Khandelwal A.(1992), Brown G.H. et al (1957), Coats D. et al (1972), Ennulat R.D.(1967), Shukla J.P. et al (1992), Shukla J. et al (1990), Gray G.W.(1962), Sackmann H. et al (1969), Sackmann H. et al (1966) and Saupe A.(1968)] and/orthermal properties [Coats D. et al (1972), Ennulat R.D.(1967), Shukla J.P. et al (1992), Shukla J. et al (1990), Gray

Corresponding Author:-Sanjai Misra
Address**:-**Department of Physics, B.S.N.V.P.G.College, Lucknow, 226001, U.P., India.

G.W.(1962), Sackmann H. et al (1969), Shri Singh (2000), Kaushlendra A. et al (2018), Tripti V. et al (2019), Davidson P. et al (2018), Aradhana R. et al (2020)]. Sometimes optical technique yield ambiguous results [Coats D. et al (1972)]. Itis therefore important to rely on other techniques and the thermalmethods, for detecting the phase transition involving subtle changes inthe molecular order, have been found to be highly sensitive and have been widely used.

Among the various methods used to study the molecularordering and molecular motion of mesophases in liquid crystals, theEPR spin probe technique has proven to be very useful in elucidatingdynamic and structural characteristics of these ordered mesophase [Meiroviteh E. et al (1982)].In the initial applications of EPR to this field, the emphasis was on themore fluid nematicand smectic phases where molecular motion is rapidand ordering is often relatively low. A major effect is observed on spinrelaxation upon passing from the isotropic to the nematic phase is theonset of molecular ordering [Polnaszek G.E. et al (1979)]. The transition from the nematic toasmectic is also reflected mainly in changes in molecular orderingcharacteristics.The dielectric anisotropy in liquid crystals resulting from theangular correlation between the molecules not only throws light on themolecular structure but also on their ordering in the mesophase which ischaracterized by the order parameter [Chandrashekhar S.(1977), Poter R.S. et al (1969), De Gennes P.G.(1974),Bauman D. et al (1995) and Miyajima S. et al (1995)]. The order parameter(s) is the single most important parameter of the liquid crystalwhich governs nearly all its physical properties. The knowledge oforder parameter and its temperature dependence is also important fromtechnological point of view [De Gennes P.G.(1974),Bauman D. et al (1995), Miyajima S. et al (1995) andGray G.W.(1976)]. There have been several studies inthe nematic phase of liquid crystals [Zaboli M. et al (1992), De Jeu W.H.(1978), Garg A.K. et al (1983), Buka A. et al (1986), Agarwal V.K. et al (1983) and Chrusciel J. et al (1992)]. It is with this in viewthat investigations on order parameter S for two liquid crystalline materialsand their mixtures by weight using EPR technique has been carried outand reported in this paper. The successive phase transitions are alsostudied.There have been several dielectric studies [Arora V.P. et al (1995) and Schinichi Y. et al (1984)] on liquid crystals and it has been reported that phase transitions can be detected using temperature dependent dielectric constant data. Therefore thephase transitions are also studied, using dielectric data by measuringdielectric permittivity as a function of temperature andfrequency, whichis further supported by the data observed using differential thermalanalysis (DTA). The results of phase transition temperatures observedfrom the above three techniques dielectric, EPR and DTA are compared.The present papertherefore reports the phase transitionstudies of two liquid crystals, namely cholesteryl palmitate and cholesteryldecanoate and their mixtures by weight, $P_{1/4}D_{3/4}$(25% cholesterylpalmitate and 75% cholesteryl decanoate) and $P_{1/2}D_{1/2}$ (50% cholesterylpalmitate and 50% cholesteryl decanoate).

Experimental Details

In order to conduct the dielectric studies, measurement ofdielectric permittivity of each sample were carried out in thetemperature range of 40-110°C in the frequency range of 1-10 kHzusing 1620-APGR capacitance measuring assembly.The cell (effective capacitance: 4.5 pf), filled with the sample,was first heated till the sample becomes isotropic liquid and then cooleddown to room temperature. The values of capacitance were thenmeasured at different temperatures while heating the sample atfrequencies 1, 2, 5 and 10 kHz and from these the dielectric permittivities (ϵ') were evaluated.For evaluating the order parameter(s), the three line EPR spectraat varying temperature were taken for all the samples using E-line Centuryseries EPR spectrometer (X-band, Model 109). By measuring thehyperfine parameter <a>in non-isotropic phase, S was evaluated andwas plotted against temperature.Further the differential thermal analysis (DTA) were carriedout for the samples at a heating rate of 2°C per minute above roomtemperature up to 150°C, using DTA-50, Shimadzu Corporation, Japan.Figs(1- 4) show the variation of dielectric constant withtemperature for respective samples at different frequencies. Fig5shows the EPR spectrum for cholesteryl palmitate at temperatures 58and 83°C. Fig 6 represents the variation of order parameter withtemperature for cholesteryl palmitate. Figs (7-10) show transitionpeaks obtained by DTA for cholesteryl palmitate, cholesteryl decanoateand their two mixtures. Table-1reports the comparative values oftransition temperatures observed from the three techniques and Table-2 gives the values of order parameter for all the samples investigated.

Discussion:-

Dielectric Measurement

The dielectric permittivity components (ϵ') of the two liquidcrystalline materials viz. cholesteryl palmitate and cholesteryl decanoateand their two mixtures $P_{1/4}D_{3/4}$ and $P_{1/2}D_{1/2}$ obtained by dielectricstudies, were plotted as a function of temperature, as shown in Figs.(1- 4), there is a marked variation in ϵ' with temperature. It has beenreported earlier that the magnitude of dielectric constant is very muchdependent on the orientation of the liquid crystal molecules, i.e. whetherthe long axis is parallel (ϵ_{II}) or perpendicular (ϵ_{T}) to the applied electricfield [Takezoe H. et al (1984)]. Any structural change which affects the molecular orientationwilltherefore necessarilyalter the dielectric constant (and hence thecapacitance of the cell) which is detected. It was for this reason thatno attempt was made to align the liquid crystals and run the risk ofconstraining it to a particular orientation. It has also been demonstratedearlier that a wide range of phase transitions can be detected usingtemperaturedependent dielectric constant and any phase transitioninvolving a structural rearrangement can in principle be detected.

The phase transition temperatures are easily observedbythe discontinuities in these curves (Figs 1-4). For cholesteryl palmitate,the curve showing variation of ϵ’ with temperature (Fig1) shows threediscontinuities at 65, 77.5 and 87°C which correspond to three successivephase transitions. In the case of cholesteryl decanoate, the discontinuitieswere observed at 60, 75 and 95°C. When these two liquid crystallinematerials were mixed by weight, the phase transition occurred atcomparatively lower temperatures. For $P_{½}D_{½}$the phase changeoccurredat 45, 70 and 85°C while in $P_{¼}D_{¾}$ it occurred at 45, 67 and 85°C.

In the case of all the four samples when they are heated aboveroom temperature, the first two transition temperatures correspond to thephase change from solid to smectic and smectic to cholesteric while the third transition occurs from Cholesteric to isotropic. In the case ofthe two mixtures, it is observed that the transition takes place at lowertemperature than that of the pure liquid crystalline materials. Also forboth the mixtures, solid to smectic and cholesteric to isotropic transitionsappear at the same temperature. However, when the amount ofcholesteryldecanoate is increased in the mixture (as in$P_{¼}D_{¾}$)the smectic tocholesteric transition temperature further decreases. It hasbeen furtherobserved that in all the systems the value of dielectricconstant increaseswith decrease in temperature. This indicates considerable freedom ofdipole orientation. In the solid phase, ϵ’ has been found to decreasewith decreasing temperature. This indicates that the orientation of thedipoles is restricted as it approaches solid phase. The fact that the values of dielectric constant at 10 kHz are lessthan those at 1 kHz indicates that the materials under investigation showdielectric dispersion at these frequencies. However, complete dispersionis likely to be obtained if measurements are taken beyond 10 kHz. Thisbehaviour of the above liquid crystalline materials and their mixtures issimilar to those observed for other liquid crystals [Kressf H. et al (1991), Arora V.P. et al (1997), Bahadur B. (ed.), (1994), Baessier H., et al (1970), Agarwal V.K. et al (1990), Gouda F. (1994) and Srivastava S.L, et al (1983)].

Electron Paramagnetic Resonance (EPR) Measurements

In the EPR spectrum, on passing from the amorphous isotropicphase to the nematic phase, the number of lines observed does notchange. Instead the spacing between the lines changes(Fig5).Therefore, a determination of the line spacing or their position providesinformation about the Order parameter.The order parameter is calculatedfrom the expression

$$S = \frac{< a > -a}{A - a}$$

Here ‘a’ is scalar hyperfine interaction and can be determined from themeasurements in the isotropic phase. Also<a> is a hyperfineparameterin non-isotropic phase and can be determined at varying temperature. ‘A’is a constant for particular probe used.In the present work, nitroxide (N→0)is used as a paramagneticspin probe for whichA=30.8 G and a=14.7G. The order parameter(S)was evaluated for the samples at various temperatures from EPR spectra.The values of S are plotted as a function of temperature (Fig6). Thediscontinuities in the curve correspond to change of phase. Thereforefrom the curve phase transition temperatures were measured. Forcholesteryl palmitate the change of phase takes place at 65, 77 and 87°Cwhile in the case of cholesteryl decanoate only two transitiontemperatures76 and 95°C were detected. Similarly for $P_{½}D_{½}$ and $P_{¼}D_{¾}$ phasechange takesplace at 70, 85°C and 67, 85°C respectively. Thesetransition temperatures obtained using EPR spectrum are in excellentagreement with those obtained from dielectric measurement. However,in the case of above mixtures one of the phases observed using EPR ismissing.

Differential Thermal Analysis (DTA) Measurement

The DTA study on pure cholesteryl palmitate and cholesteryldecanoate has clearly identified the transition peaks at 65.3, 77.94, 86.44°Cand 59.25, 75.23, 94.31°C respectively for the two liquid crystallinematerials. While two mixtures $P_{½}D_{½}$and $P_{¼}D_{¾}$yield transition peaksat 45.14, 69.85, 84.88°C and 45, 66.38, 84.38°C respectively (Figs 7-10). These transition temperatures are again in good agreement withthose obtained by other techniques.

Conclusion:-

The phase transition temperatures observed for the twoliquid crystalline materials and their mixtures from three techniques viz.dielectric, EPR and DTA are given in Table-1. The transitiontemperatures observed from these techniques are in excellent agreementwith each other. However, the values of pure materials differ slightlyfrom literature values which might be because of some impurity in thesamples.

Table 1:- Phase transition temperatures using three techniques for two liquid crystals and their mixtures.

Material	**From dielectric data °C**	**From EPR data °C**	**From DTA data °C**
Cholesteryl Palmitate	65	65	65.30
	77.5	77	77.94
	87	87	86.44
Cholesteryl decanoate	60	-	59.25
	75	76	75.23
	95	95	94.31
$P_{1/4}D_{3/4}$	45	-	45.00
	67	67	66.38
	85	85	84.38
$P_{1/2}D_{1/2}$	45	-	45.14
	70	70	69.85
	85	85	84.88

Table 2:- Variation of order parameter ($S \times 10^2$) with temperature.

Cholesteryl Palmitate		**Cholesteryl decanoate**		$\boldsymbol{P_{1/4}D_{3/4}}$		$\boldsymbol{P_{1/2}D_{1/2}}$	
Temp **°C**	order parameter ($S \times 10^2$)	Temp **°C**	order parameter ($S \times 10^2$)	Temp **°C**	order parameter ($S \times 10^2$)	Temp **°C**	order parameter ($S \times 10^2$)
53	9.7	61	12.2	44	12.2	49	10.6
58	8.4	67	10.9	49	10.9	53	9.7
61	7.3	72	9.7	56	9.7	58	8.4
63	6.2	76	8.7	61	8.5	63	6.8
65	4.0	77	6.1	65	7.3	67	5.3
70	3.6	79	5.6	67	6.7	70	3.7
73	3.4	81	5.0	69	4.0	72	3.7
77	3.2	83	4.5	72	3.7	77	3.2
83	1.2	87	3.3	79	2.4	80	2.6
87	0.0	90	2.3	83	1.2	83	1.4
94	0.0	92	1.4	85	0.0	85	0.0
100	0.0	94	0.6	92	0.0	89	0.0
105	0.0	95	0.0	-	-	-	-
-	-	100	0.0	-	-	-	

Acknowledgement:-

I wish to acknowledge Dr A. Kumar, Professor, Department of Physics, H.B.T.I., Kanpur and Dr.Prem Chand, Incharge EPR Laboratory, I.I.T., Kanpur, for providing experimental facilities. I would thank Prof J.P. Shukla and Prof Manisha Gupta, Department of Physics, Lucknow University for their suggestions and support. I would also like to thank Sri Indresh Kumar Shukla for typing the manuscript in prescribed format.

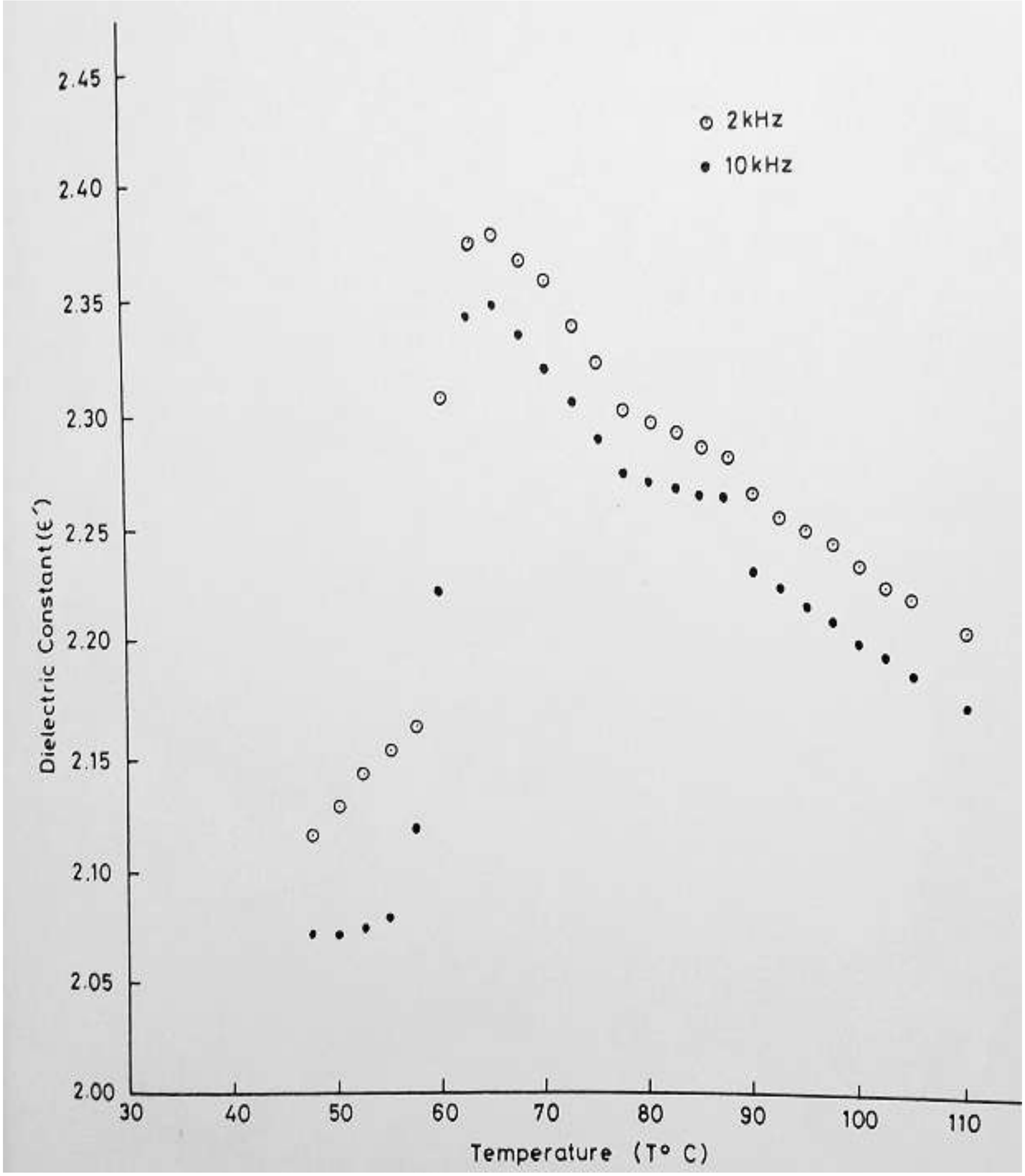

Fig1:- Plot of ϵ' versus T for Cholesteryl Palmitate.

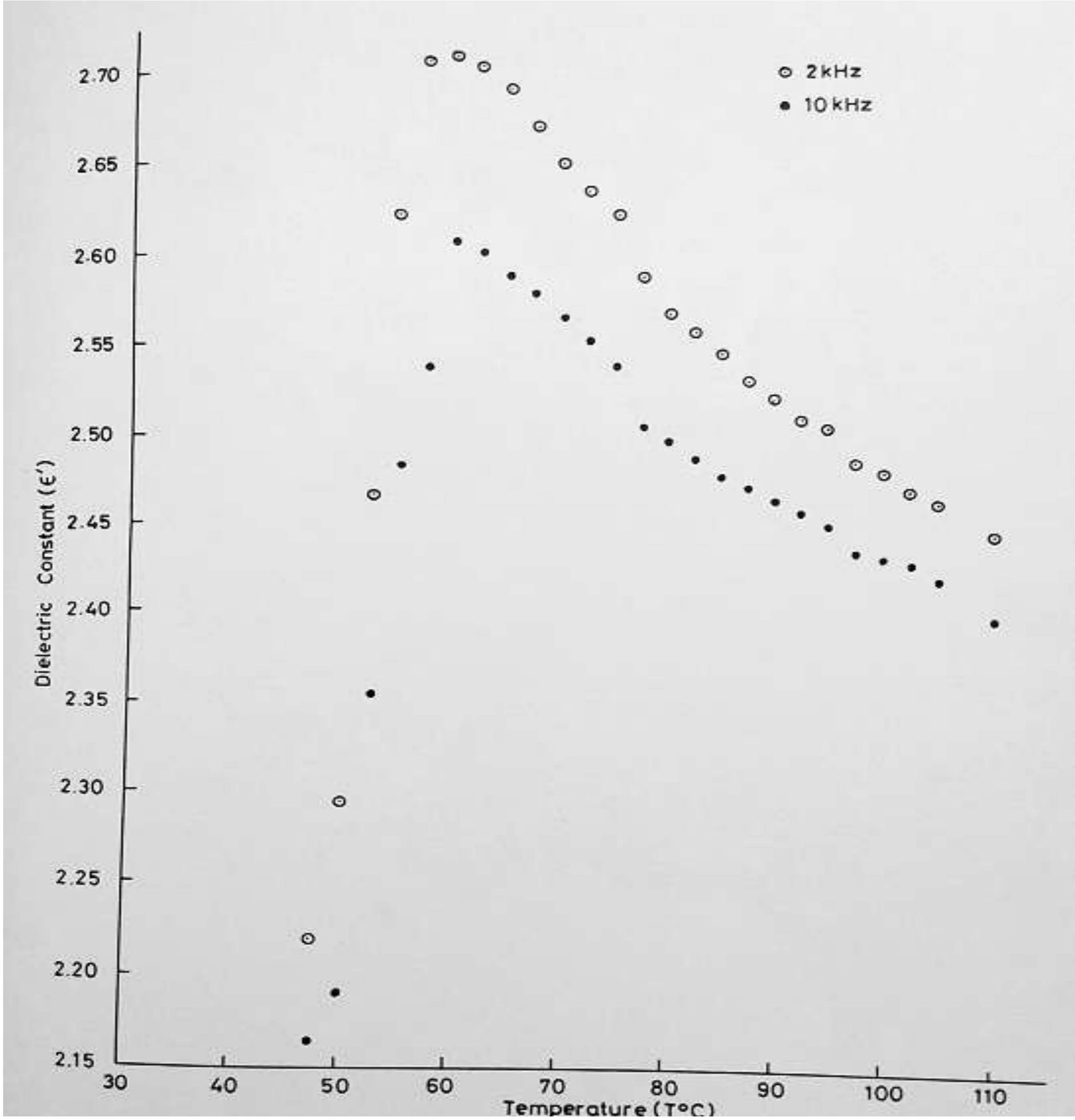

Fig2:- Plot of є' versus T for Cholesteryl Decanoate.

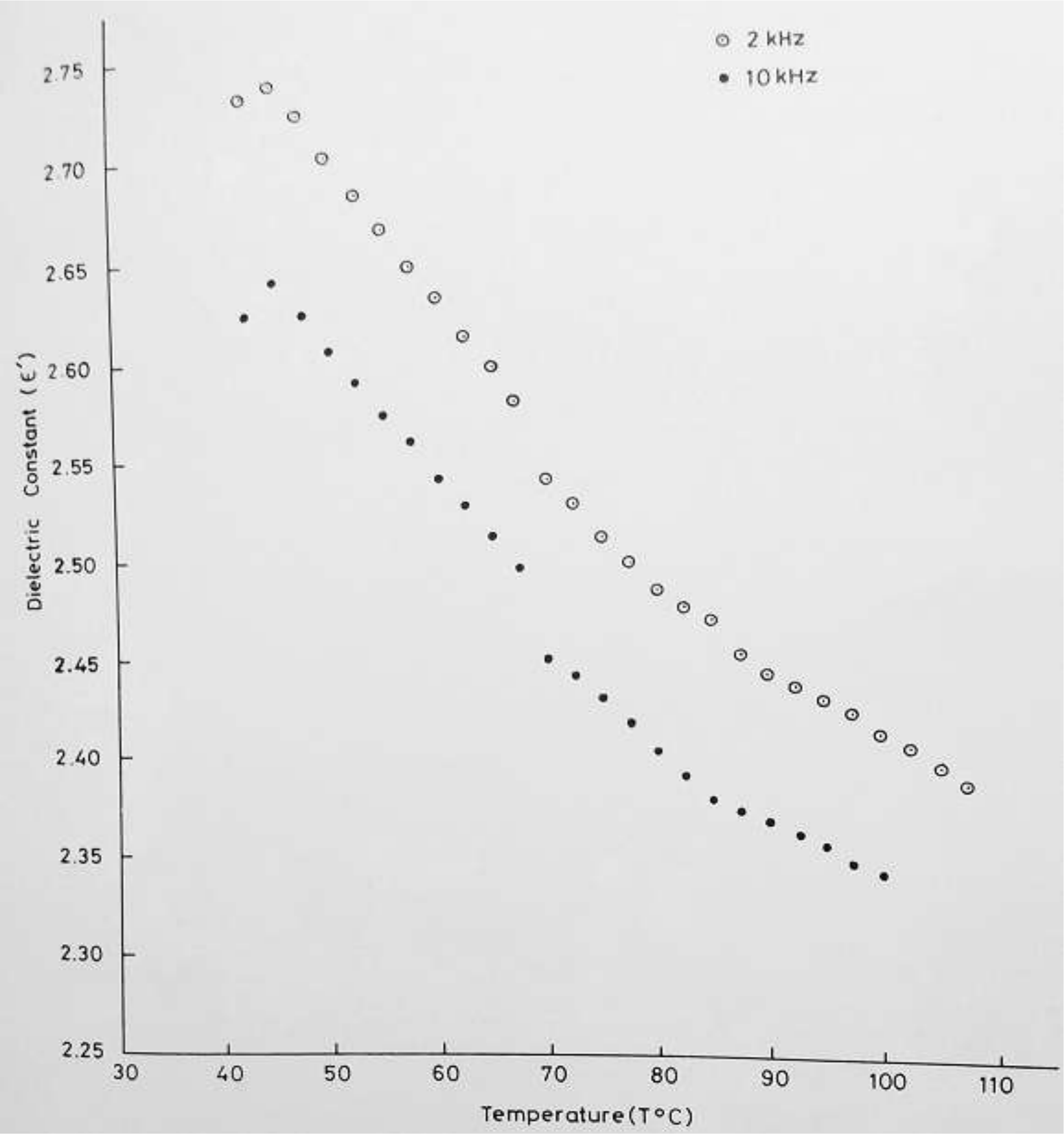

Fig3:- Plot of ϵ' versus T for $P_{1/4}D_{3/4}$

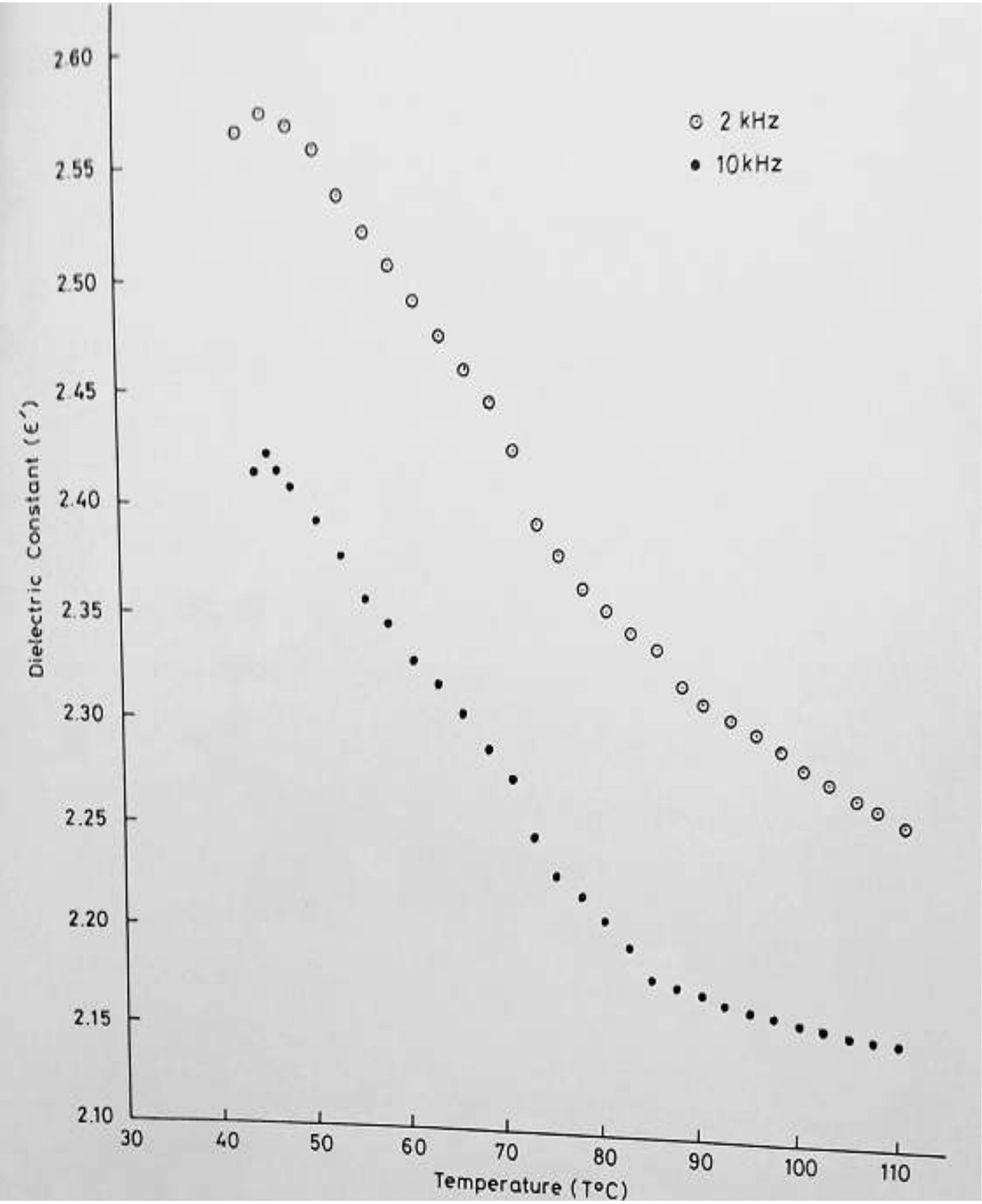

Fig 4:-Plot of ϵ’ versus T for $P_{1/2}D_{1/2}$.

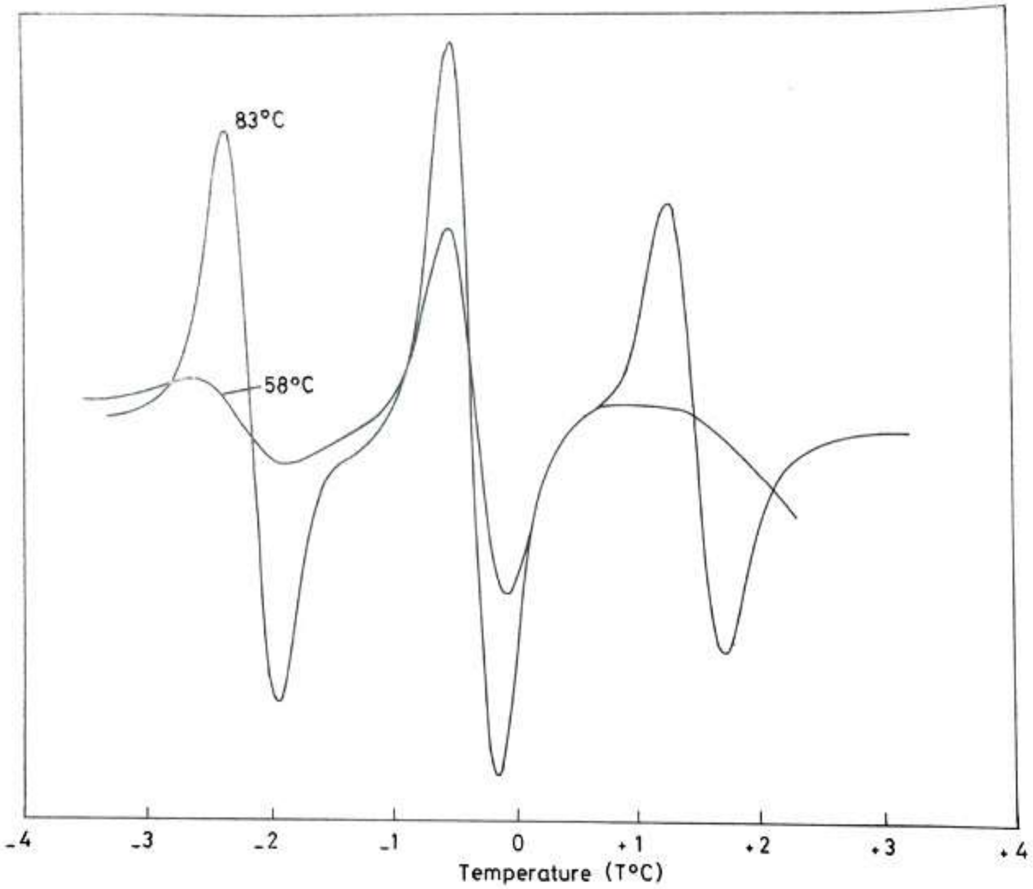

Fig 5:- Three line EPR spectrum of Cholesteryl Palmitate at temperatures 58**°C** and 83**°C.**

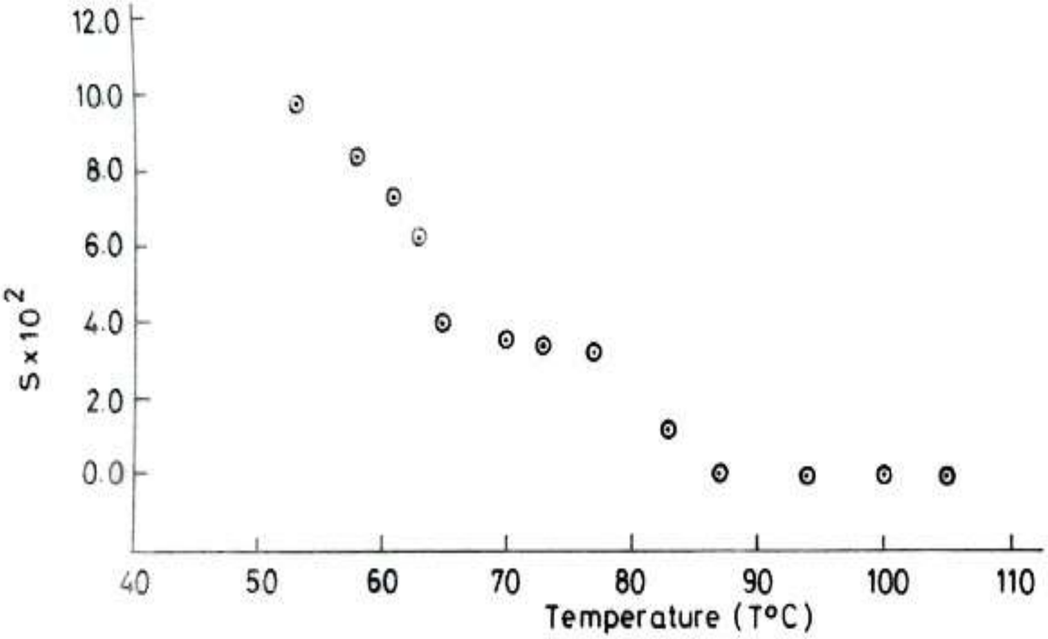

Fig 6:- Variation of order parameter (S) with temperature for Cholesteryl Palmitate.

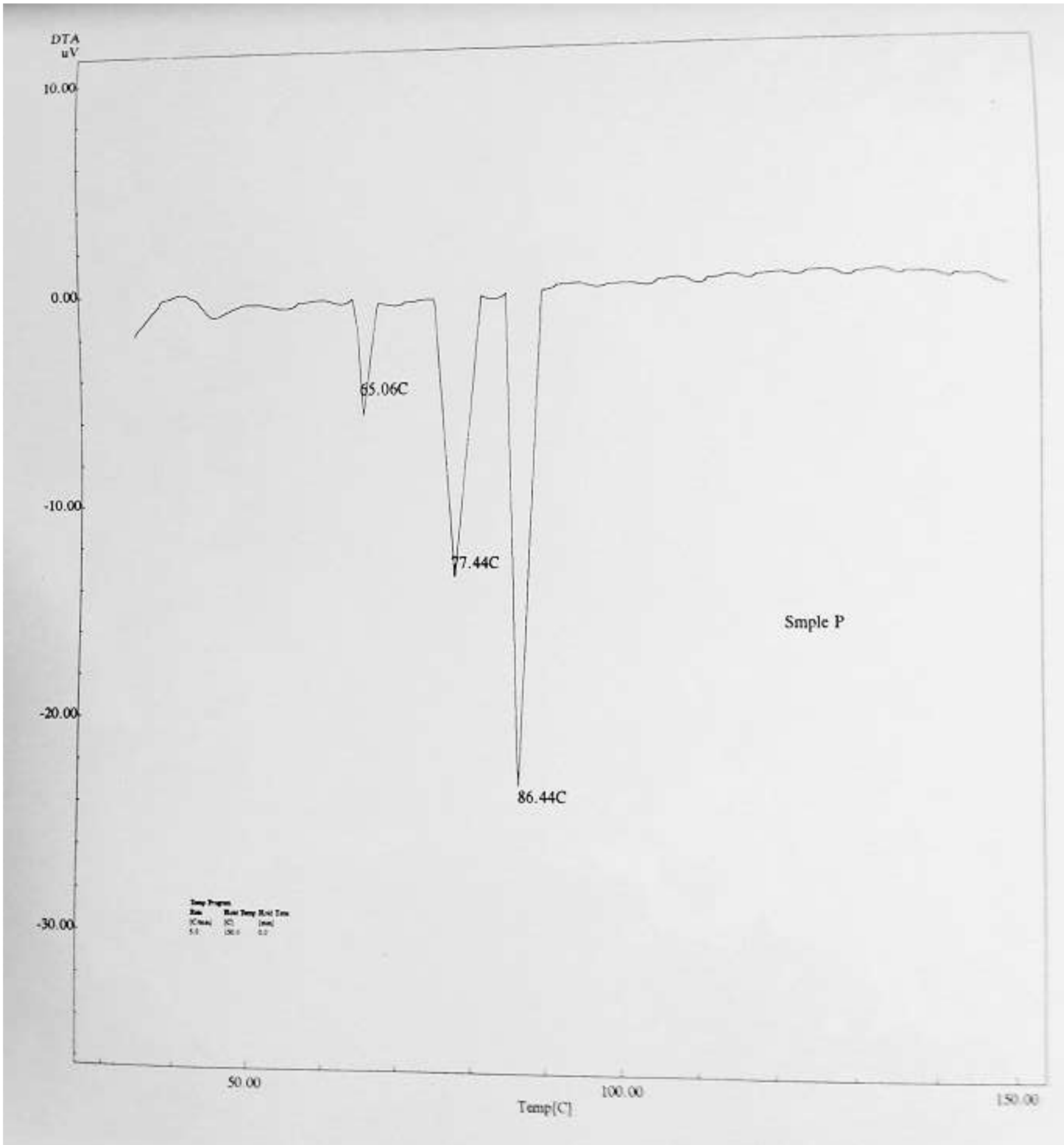

Fig7:-DTA Curve of Cholesteryl Palmitate.

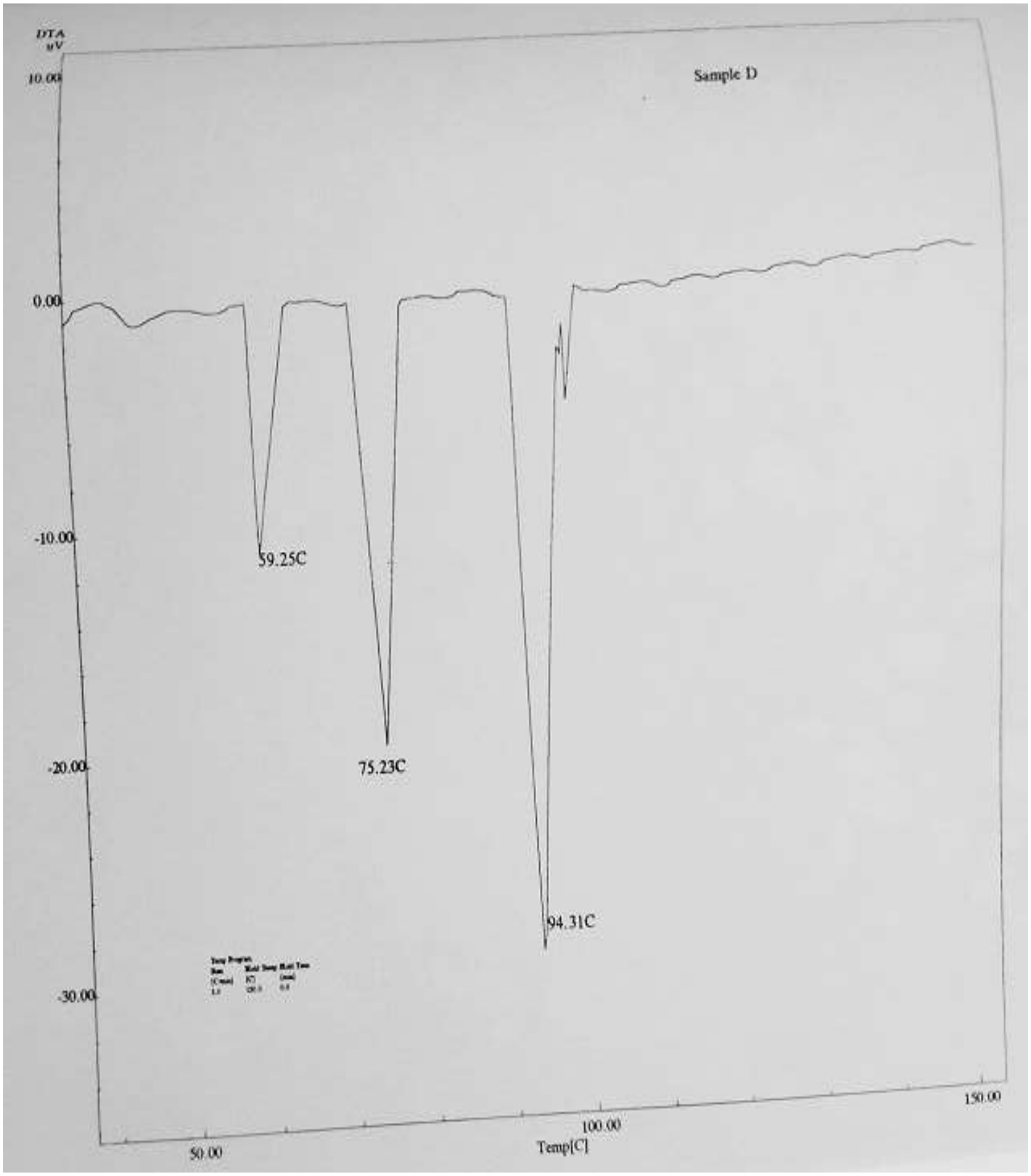

Fig8:- DTA Curve of Cholesteryl Decanoate.

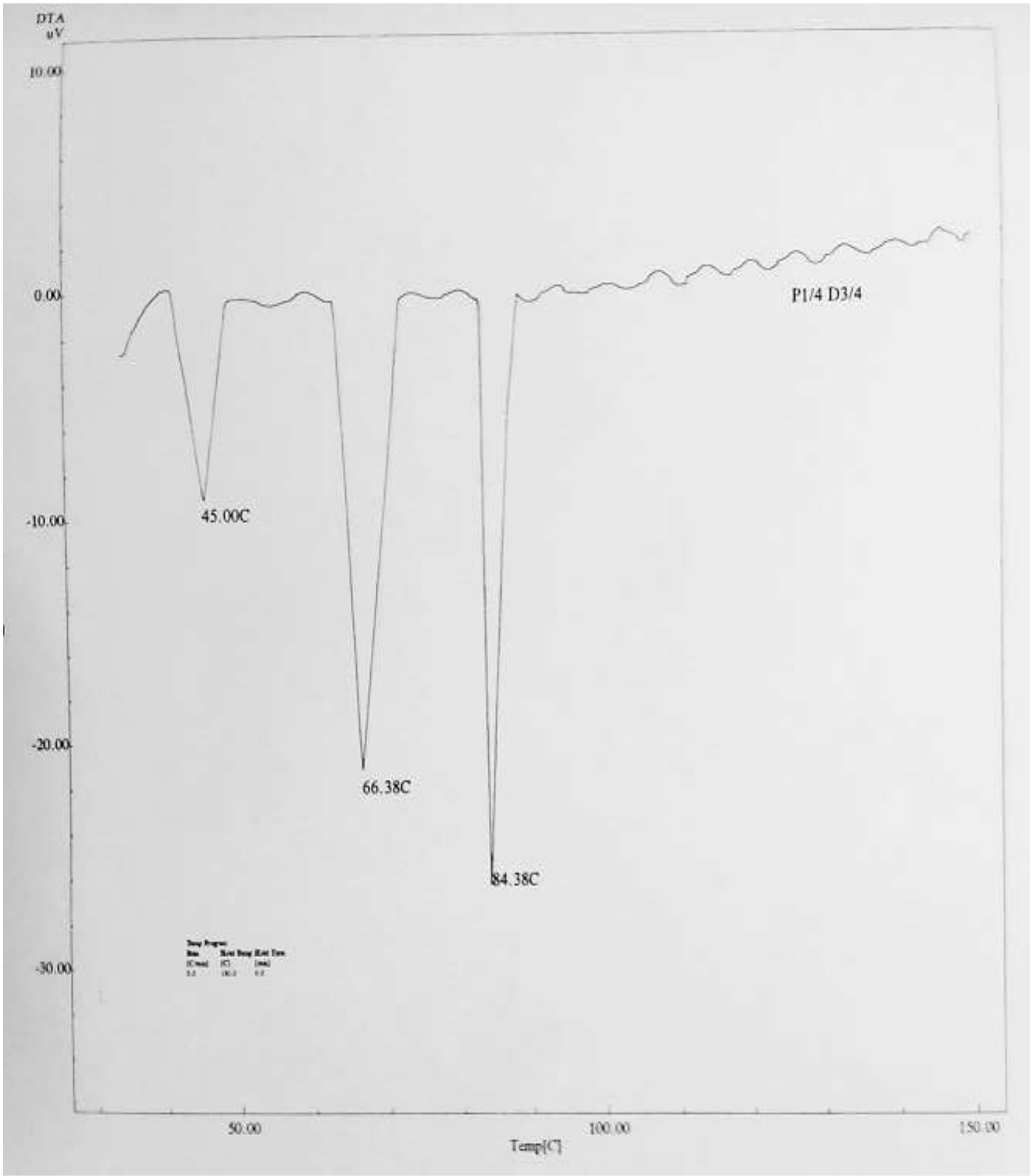

Fig 9:- DAT Curve of $P_{1/4}D_{3/4}$

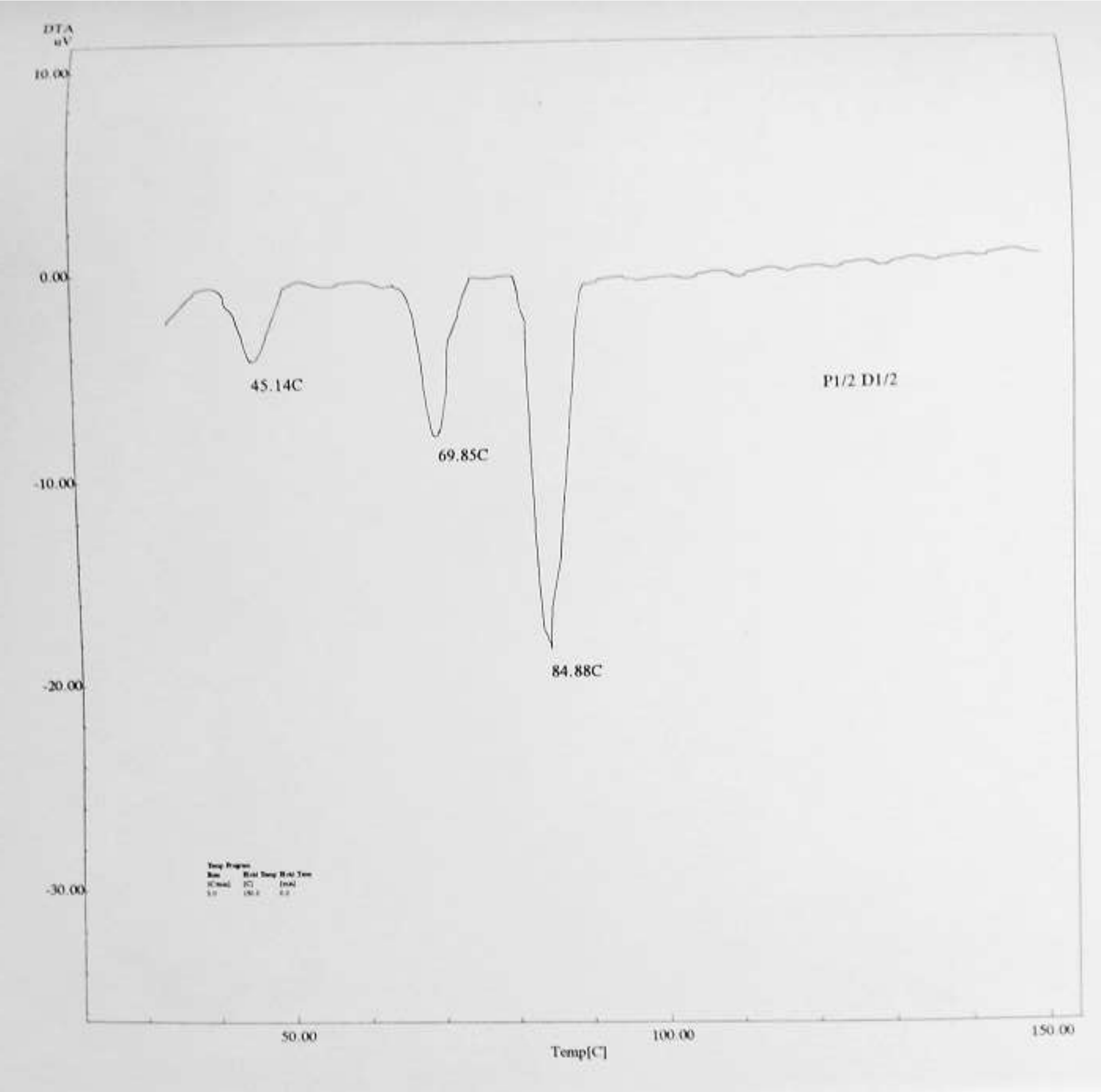

Fig 10:- DTA Curve of $P_{1/2}D_{1/2}$

References:-

1. Agarwal V.K. and Price A.H.(1983), Mol. Cryst. Liq. Cryst. 98, 193
2. Agarwal V.K., Shukla J.P., Arora V.P. and Elamen S.M.(1990), Nat. Acad.Sei. Lett. 13 (12), 453.
3. Aradhana R, Tripathi PK, Mahabaleshwara s, Srinivasulu M, Gangwar R K and RajiveManohar (2020), Optical materials, Vol 107, Sept 2020, 110021
4. Arora V.P., Kumar A. and Agarwal V.K.(1995), Indian J. Phys. 69(A) (0),665.
5. Arora V.P., Kumar A. and Agarwal V.K.(1997), Indian J. Phys. 71A(5),579.
6. Baessier H., Beard R.B. and Labes M.M.(1970), J. Chem. Phys. 52, 2292.
7. Bahadur B. (ed.), (1994), Liquid Crystals: Applications and uses, Vol. 1-11,Singapore: World Scientific.
8. Bauman D., Martynski T. and MykOwska E.(1995), Liq. Cryst,, 18(4),607.
9. Brown G.H. and Shaw W.G.(1957), Chem. Rev. 57, 1049.
10. Brown G.H., Doans J.W. and Neff V.D.(1971), A review of the structureand physical properties of liquid crystals, Cleveland, Ohio: CRCPress .
11. Buka A. and Bata L.(1986), Mol. Cryst. Liq. Cryst. 135, 49.
12. Chandrashekhar S.(1977), Liquid Crystals, Cambridge University Press,Cambridge.

13. Chrusciel J., Kresse H. and Urban S.(1992), Liq. Cryst., 11,711.
14. Coats D., Harrison K.J. and Gray G.W.(1972), Proc. 4th Internatl. ConfLiq. Cryst.,Kenth State University, Kenth, Ohio, Abstract No. 109.
15. Davidson P, Penisson C, Constantin D, Gabriel JP (2018), Proceedings of the National Academy of Sciences of the United States of America, 115 (26): 6662-6667
16. De Gennes P.G.(1974), The Physics ef Liquid Cystals, Clarendon Press,London.
17. De Jeu W.H.(1978), Dielectric Permittivity of liquid crystal, Solid StatePhysics, Suppl. 14, 109.
18. Ennulat R.D.(1967), Mol. Cyst. Liq. Cyst. 56, 107.
19. Garg A.K., Gupta G.K., Arora V.P., Agarwal V.K. and Bahadur B.(1983),Mol. Cryst. Liquid Cryst. 103, 205
20. Gouda F.(1994), Liq. Cryst. 17, 367.
21. Gray G.W.(1962), Mol. Structure and Properties of the Liquid Crystal,New York: Academic.
22. Gray G.W.(1976), Advances in Liquid Cystals, Vol. 1, Academic Press,N.Y.
23. HillN.E.,VaughanW.E., PriceA.H. and DavisM.,(1969), Dielectricproperties and molecular behaviour, Von Nostrand Reinhold Co,London; SmithC.P.(1953)., Dielectric behaviour and structure,McGraw Hill, N. Y.
24. Kaushlendra A, Govind P, Tripti V, Katarzyna K, Srivastava A and Rajiv Manohar (2018), Journal of Molecular Liquids, Vol 264, 15 August 2018, p510-514
25. Khandelwal A.(1992)., Ind. J. Pure and Appl. Phys, 30, 127
26. Kressf H., Hartmann P., Schafer W. and Szulzewsky L.(1991), Liq. Cryst.,10(1), 127.
27. Meiroviteh E., Igner D., Igner E., Moro G. and Freed J.H.(1982), J. Chem.Phys. 77 (7), 3915.
28. Miyajima S., Nakazato A., Sakoda N. and Chiba T.(1995), Lig. Cryst, 18(4), 651.
29. Nagappa, Ravannasiddaiah D. and Marthandappa M.(1991), Ind. J. Phys.65(A), 246.
30. Polnaszek G.E. and Freed J.H.(1979), J. Phys. Chem. 79, 2283 (1975);W.J. Lin and J.H. Freed, lbid, 83, 379
31. Poter R.S., Barrall E.M. and Johnson J.E.(1969), Ac. Chem. Res. 2, 53.
32. Sackmann H. and Demus D.(1966), Mol. Cryst., 2, 81.
33. Sackmann H. and Demus D.(1969), Fortschr Chem. Forsch 12, 349.
34. Saupe A.(1968), Angew. Chem. Int. Ed. (English) 7, 97.
35. Schinichi Y., Naotake N., Yukio Y. and Kohji S.(1984), Mol. Cryst. Liq.Cryst. 108, 277.
36. Shri Singh (2000), Physics Reports ,vol 324, issue (2-4), Feb 2000, page 107-269
37. Shukla J. and Suri S.K.(1990), Ind.J. Phys., 64A, 485.
38. Shukla J.P., Agarwal V.K., Ali J.A. and Arora V.P.(1992), Nat. Acad. Sci.Lett., 15(3), 77.
39. Srivastava S.L., Suri S.K. and Gouda F.M.(1983), Nat. Acad. Sci. Lett. 6(11), 351
40. Takezoe H., Kondo K., Mitasato K., Abe S., Tsuchiya T., Fupuda A. and Kuze E.(1984), Ferroelectrics 58, 55.
41. Tripti V, Kaushlendra A, Sonkar R K, RajiveManohar (2019), Journal of Molecular Liquids, Vol 290,15 Sept 2019, 111241
42. Zaboli M., Kafle S.R., Saran D. and Jain P.C.(1992), Ind. J. Phys. 66A(5),583.