RESEARCH ARTICLE

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

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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.

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 occurs within a certain range of temperature in melts and solutions of many organic compounds. The ordering is sufficient to impart some solid-like properties to the fluid but the forces of attraction usually are not strong enough to prevent flow. The term liquid crystal thus refers to the phase that lies between the rigidly ordered solid phase where the mobility of individual molecule is restricted and the isotropic phase where molecular mobility and a general lack of molecular order exist. As a result, there is anisotropy in the mechanical, electrical and optical properties. The dielectric and optical studies of liquid crystal are important as they provide information about molecular structure, intermolecular forces and molecular dynamics [Hill N.E. et al (1969)]. Structural changes arising from the transition between the mesophases of liquid crystalline materials are generally studied using optical properties [Brown G.H. et al (1971), Nagappa et 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 Sauer A.(1968)] and/or thermal properties [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), 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)]. It’s therefore important to rely on other techniques and the thermal methods, for detecting the phase transition involving subtle changes in the molecular order, have been found to be highly sensitive and have been widely used.

Among the various methods used to study the molecular ordering and molecular motion of mesophases in liquid crystals, the EPR spin probe technique has proven to be very useful in elucidating dynamic and structural characteristics of these ordered mesophase [Meirovitch E. et al (1982)]. In the initial applications of EPR to this field, the emphasis was on the more fluid nematic and smectic phases where molecular motion is rapidand ordering is often relatively low. A major effect is observed on spin relaxation upon passing from the isotropic to the nematic phase is the onset of molecular ordering [Polnaszek G.E. et al (1979)]. The transition from the nematic to the smectic is also reflected mainly in changes in molecular ordering characteristics. The dielectric anisotropy in liquid crystals resulting from the angular correlation between the molecules not only throws light on the molecular structure but also on their ordering in the mesophase which is characterized 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 crystal which governs nearly all its physical properties. The knowledge of the order parameter and its temperature dependence is also important from technological point of view [De Gennes P.G. (1974), Bauman D. et al (1995), Miyajima S. et al (1995) and Gray G.W. (1976)]. There have been several studies into the nematic phase of liquid crystals [Zaboli M. et al (1992), De Jeu W.H. (1978), Garg A.K. et al (1983), Bukar A. et al (1986), Agarwal V.K. et al (1983) and Chrusciel J. et al (1992)]. It is with this in view that investigations on order parameter S for two liquid crystalline materials and their mixtures by weight using EPR technique has been carried out and reported in this paper. The successive phase transitions are also studied. 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 the phase transitions are also studied, using dielectric data by measuring dielectric permittivity as a function of temperature and frequency, which is further supported by the data observed using differential thermal analysis (DTA). The results of phase transition temperatures observed from the above three techniques dielectric, EPR and DTA are compared. The present paper therefore reports the phase transition studies of two liquid crystals, namely cholesterol palmitate and cholesterol decanoate and their mixtures by weight, \( P_{50}D_{50} \) (25% cholesterol palmitate and 75% cholesterol decanoate) and \( P_{50}D_{50} \) (50% cholesterol palmitate and 50% cholesterol decanoate).

**Experimental Details**

In order to conduct the dielectric studies, measurement of dielectric permittivity of each sample were carried out in the temperature range of 40-110°C in the frequency range of 1-10 kHz using 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 cooled down to room temperature. The values of capacitance were then measured at different temperatures while heating the sample at frequencies 1, 2, 5 and 10 kHz and from these the dielectric permittivities (\( \varepsilon' \)) were evaluated. For evaluating the order parameter(s), the three line EPR spectra at varying temperature were taken for all the samples using E-line Centurys series EPR spectrometer (X-band, Model 109). By measuring the hyperfine parameter \( <a> \) in the non-isotropic phase, S was evaluated and was plotted against temperature. Further the differential thermal analysis (DTA) were carried out for the samples at a heating rate of 2°C per minute above room temperature up to 150°C, using DTA-50, Shimadzu Corporation, Japan. Figs 1-4 show the variation of dielectric constant with temperature for respective samples at different frequencies. Fig 5 shows the EPR spectrum for cholesterol palmitate at temperatures 58 and 83°C. Fig 6 represents the variation of order parameter with temperature for cholesterol palmitate. Figs 7-10 show transition peaks obtained by DTA for cholesterol palmitate, cholesterol decanoate and their two mixtures. Table 1 reports the comparative values of transition 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 (\( \varepsilon' \)) of the two liquid crystalline materials viz. cholesterol palmitate and cholesterol decanoate and their two mixtures \( P_{50}D_{50} \) and \( P_{50}D_{50} \) obtained by dielectric studies, were plotted as a function of temperature, as shown in Figs. (1-4), there is a marked variation in \( \varepsilon' \) with temperature. It has
been reported earlier that the magnitude of dielectric constant is very much dependent on the orientation of the liquid crystal molecules, i.e. whether the long axis is parallel ($\epsilon_{||}$) or perpendicular ($\epsilon_{\perp}$) to the applied electric field. Any structural change which affects the molecular orientation will therefore necessarily alter the dielectric constant and hence the capacitance of the cell, which is detected. It was for this reason that no attempt was made to align the liquid crystals and run the risk of constraining it to a particular orientation. It has also been demonstrated earlier that a wide range of phase transitions can be detected using temperature dependent dielectric constant and any phase transition involving a structural rearrangement can in principle be detected.

The phase transition temperatures are easily observed by the discontinuities in these curves (Figs 1-4). For cholesteryl palmitate, the curve showing variation of $\epsilon'$ with temperature (Fig 1) shows three discontinuities at 65, 77.5 and 87°C which correspond to three successive phase transitions. In the case of cholesteryl decanoate, the discontinuities were observed at 60, 75 and 95°C. When these two liquid crystalline materials were mixed by weight, the phase transition occurred at comparatively lower temperatures. For $P_{90}D_{10}$, the phase change occurred at 45, 70 and 85°C while in $P_{90}D_{20}$ it occurred at 45, 67 and 85°C.

In the case of all the four samples when they are heated above room temperature, the first two transition temperatures correspond to the phase change from solid to smectic and smectic to cholesteric while the third transition occurs from Cholesteric to isotropic. In the case of the two mixtures, it is observed that the transition takes place at lower temperature than that of the pure liquid crystalline materials. Also for both the mixtures, solid to smectic and cholesteric to isotropic transitions appear at the same temperature. However, when the amount of cholesteryl decanoate is increased in the mixture (as in $P_{50}D_{50}$), the smectic to cholesteric transition temperature further decreases. It has been further observed that in all the systems the value of dielectric constant increases with decrease in temperature. This indicates considerable freedom of dipole orientation. In the solid phase, $\epsilon'$ has been found to decrease with decreasing temperature. This indicates that the orientation of the dipoles is restricted as it approaches solid phase. The fact that the values of dielectric constant at 10 kHz are less than those at 1 kHz indicates that the materials under investigation show dielectric dispersion at these frequencies. However, complete dispersion is likely to be observed if measurements are taken beyond 10 kHz. This behaviour of the above liquid crystalline materials and their mixtures is similar to those observed for other liquid crystals.

Electron Paramagnetic Resonance (EPR) Measurements
In the EPR spectrum, on passing from the amorphous isotropic phase to the nematic phase, the number of lines observed does not change. Instead the spacing between the lines changes (Fig 5). Therefore, a determination of the line spacing or their position provides information about the order parameter. The order parameter is calculated from the expression

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

Here ‘$a$’ is scalar hyperfine interaction and can be determined from the measurements in the isotropic phase. Also $<a>$ is a hyperfine parameter in a 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 paramagnetic spin probe for which $A = 30.8$ G and $a = 14.7$ G. 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 (Fig 6). The discontinuities in the curve correspond to change of phase. Therefore from the curve phase transition temperatures were measured. For cholesteryl palmitate the change of phase takes place at 65, 77 and 87°C while in the case of cholesteryl decanoate only two transition temperatures 76 and 95°C were detected. Similarly for $P_{40}D_{40}$ and $P_{90}D_{10}$, phase change takes place at 70, 85°C and 67, 85°C respectively. These transition temperatures obtained using EPR spectrum are in excellent agreement with those obtained from dielectric measurement. However, in the case of above mixtures, one of the phases observed using EPR is missing.

Differential Thermal Analysis (DTA) Measurement
The DTA study on pure cholesteryl palmitate and cholesteryl decanoate has clearly identified the transition peaks at 65.3, 77.94, 86.44°C and 59.25, 75.23, 94.31°C respectively for the two liquid crystalline materials. While two mixtures $P_{90}D_{10}$ and $P_{50}D_{50}$ yield transition peaks at 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 with those obtained by other techniques.
Conclusion:-
The phase transition temperatures observed for the two liquid crystalline materials and their mixtures from three techniques viz. dielectric, EPR and DTA are given in Table-1. The transition temperatures observed from these techniques are in excellent agreement with each other. However, the values of pure materials differ slightly from literature values which might be because of some impurity in the samples.

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_{\frac{1}{4}}D_{\frac{3}{4}} | 45                       | -                | 45.00            |
|                     | 67                       | 67               | 66.38            |
|                     | 85                       | 85               | 84.38            |
| P_{\frac{1}{2}}D_{\frac{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 | $P_{\frac{1}{4}}D_{\frac{3}{4}}$ | $P_{\frac{1}{2}}D_{\frac{1}{2}}$ |
|-----------------------|-----------------------|----------------------------------|----------------------------------|
| Temp °C               | order parameter ($S \times 10^2$) | Temp °C | order parameter ($S \times 10^2$) | Temp °C | order parameter ($S \times 10^2$) |
| 53                    | 9.7                   | 61                     | 12.2                           | 44                   | 12.2                           |
| 58                    | 8.4                   | 67                     | 10.9                           | 49                   | 10.9                           |
| 61                    | 7.3                   | 72                     | 9.7                            | 56                   | 9.7                            |
| 63                    | 6.2                   | 76                     | 8.7                            | 61                   | 8.5                            |
| 65                    | 4.0                   | 77                     | 6.1                            | 65                   | 7.3                            |
| 70                    | 3.6                   | 79                     | 5.6                            | 67                   | 6.7                            |
| 73                    | 3.4                   | 81                     | 5.0                            | 69                   | 4.0                            |
| 77                    | 3.2                   | 83                     | 4.5                            | 72                   | 3.7                            |
| 83                    | 1.2                   | 87                     | 3.3                            | 79                   | 2.4                            |
| 87                    | 0.0                   | 90                     | 2.3                            | 83                   | 1.2                            |
| 94                    | 0.0                   | 92                     | 1.4                            | 85                   | 0.0                            |
| 100                   | 0.0                   | 94                     | 0.6                            | 92                   | 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.
Fig 2: Plot of ε' versus T for Cholesteryl Decanoate.
Fig 3: Plot of $\varepsilon'$ 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.
Fig 7: 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 $P_{1/2}D_{1/2}$

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