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RESEARCH ARTICLE

STUDIES ON MOLECULAR INTERACTIONS OF LIQUID CRYSTALLINE MATERIALS USING THERMODYNAMIC AND ULTRASONIC TECHNIQUE.

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Abstract

We report the results of our studies on optical and thermal properties of ternary mixture of compounds, viz., laurylpyridinium chloride (LPC), cholesteryl nonanoate (CN) and orthophosphoric acid (H_3PO_4). These mixture exhibits a very interesting cholesteric and induced reentrant smectic-A phases for different concentrations of CN sequentially when the specimen is cooled from its isotropic phase. The temperature variations of optical-density and ultrasonic measurements have been discussed. Thermodynamical response of birefringence has also been discussed to understand: the phase stability, chemical structure and molecular dynamics of the multi-component system of liquid crystalline materials.

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Introduction:-

Generally the matter exists in three states, viz., solid, liquid and gas. Certain organic compounds show intermediate phases between crystalline solids and isotropic liquids, which are thermodynamically stable. These phases exhibit rheological behavior similar to the liquids but have anisotropic properties of crystalline solids and hence they are termed as liquid crystal phases [1-3]. Liquid crystals have been extensively investigated due to increasing importance in science and technological applications [4-7].

In the present investigation, we have shown the existence of induced reentrant smectic and cholesteric phases respectively at different concentrations in the multi-components, namely, cholesteryl nonanoate (CN), laurylpyridinium chloride (LPC) and Orthophosphoric acid (H_3PO_4). These phases have been characterized by using optical anisotropic techniques for different concentrations and at different temperatures. In light of the above investigations, an attempt has been made to understand the coupling between aggregated structure and mesophase order [8].

Experimental Studies:-

In the present study, we use the multi-component materials, namely, laurylpyridinium chloride (LPC), cholesteryl nonanoate (CN) and orthophosphoric acid (H_3PO_4). Mixtures of different concentrations of CN in $LPC+H_3PO_4$ were prepared and were mixed thoroughly and they were kept in desiccators for 6 hours. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. Phase transition temperatures of these

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mixtures were measured with the help of a polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip, and were sealed for microscopic observations. The permitted temperature control was $\pm 0.1^\circ\text{C}$. The level of liquid crystal in the capillary was read to $\pm 0.01\text{mm}$ with a cathetometer. The absolute error in the density measurements was $\Delta\rho = \pm 0.0001\text{ g/cc}$. The ultrasonic velocity was measured at 2 MHz using the ultrasonic interferometer UI 601 NPL India. The cell was essentially the same as that supplied with the interferometer except a few modifications for the heating arrangement. The temperature of the cell was controlled by controlling the current flowing through the heating element surrounding the cell. The permitted temperature control was $\pm 0.2^\circ\text{C}$. The ultrasonic velocity measurements were accurate to $\pm 0.2\%$.

Results And Discussions:-

Optical Texture Studies:-

For the purpose of optical texture studies, the sample was sandwiched between the slide and cover glass and then the optical textures were observed using Leitz-polarizing microscope in conjunction with hot stage. The concentrations ranges from 7% to 13% and 25% to 45% of the given mixture are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a fingerprint pattern of cholesteric phase with large values of pitch [9, 10]. On further cooling the specimen, the cholesteric phase slowly changes over to focal conic fan shaped texture, which is the characteristics of SmA phase as shown in Figure 1(a). On further cooling the specimen, SmA phase changes over to schlieren texture of SmC phase, which as shown in Figure 1(b). The SmC phase is unstable and then this phase changes over to bubbles in the form of battonnets, which are the characteristic of SmA phase and this phase has been termed as the reentrant SmA (ReSmA) phase. On further cooling, this phase changes over to focal conic fan shaped herring bone pattern of the SmE phase and then this phase changes over to the hexagonally highly ordered smectic-B phase, which remains stable at room temperature [11].

Density Measurement

Temperature variations of density for the sample of 11% of CN in $\text{LPC}+\text{H}_3\text{PO}_4$ as shown in the Figure 2, which clearly illustrates that: the density increases linearly with decrease of temperature in the optical region between isotropic and crystalline phase of given mixture. The phase transition is very nearer to isotropic and cholesteric phase region, in this transition at particular region a sudden jump has been observed in the values of density. A sudden jump in the value of density shows the increases its value hence it indicates that: the phase transition region in between isotropic and cholesteric phase transition is probably first order. A sudden jump in the value of density at optical region is attributed to a sudden change in the molecular structure, that they were confirmed macroscopically by microscopic technique. The higher values of density in the cholesteric phase region are more than that of in isotropic region: which clearly indicates that, the tendency of increasing molecular order is more with decrease of temperature [12, 13], the pre-transitional effects at optical region between isotropic and cholesteric phase phase transitions are found to observed on the lower side of the transition, which supported by Maier-Saupe theory [14]. After isotropic transition, at cholesteric phase region the density of given mixtures increases linearly with decrease of temperature and then at the optical region between Cho \rightarrow SmA, SmA \rightarrow SmC, SmC \rightarrow ReSmA, ReSmA \rightarrow SmE and SmE \rightarrow SmB phase transition: the values of density show an increasing nature. The measured higher value of density and thermal expansion coefficient indicate that: the phase transition is first order. Our measurements studies are in accordance with Torza and Cladis worked on the molecules CBOOA. Densities of the given mixtures are increases gradually with decrease of temperature towards the smectic-B phase. The increasing values of densities: that has been experimentally observed at different optical regions with decrease of temperature towards the crystalline phase. The measurements of increasing values of densities across at different optical regions are more predominant than one to other optical regions.

Temperature Variations Of Ultrasonic Velocity, Adiabatic And Molar Compressibility:-

The mixtures of liquid crystalline materials due to their unusual behaviors have attracted considerable attention. Ultrasonic velocity measurements also help in the study of phase behavior with temperature [15]. Orientational order of the molecules in mesomorphic/non- mesomorphic compound changes with increasing the concentration of one more additive substance and hence the attractive force between the components of the molecules, the measure of ultrasonic velocity and absorption should shows nature of attractive forces existing between the mixtures of given molecules. Data on some of the properties are associated with refractive index, ultrasonic velocities and surface tensions are used to find the extensive applications in chemical engineering process, simulation and molecular dynamics [16]. The temperature variation of ultrasonic velocity, adiabatic compressibility and molar compressibility in the present case is shown in Figures 3(a)-(c). The velocity exhibits an anomalous behavior at the isotropic-

mesophase transition while it varies linearly in the isotropic and mesomorphic phases away from transition. The velocity shows a dip at the transition. The ultrasonic velocity linearly increases in isotropic phases up to the transition with decreasing temperature [17, 18]. The increase in velocity is explained as the decrease in mean distance between the molecules, thereby increasing the potential energy of the interaction between the molecules. The velocity reaches a minimum at the transition temperature and increases sharply below the transition, and then it shows a linear increase in mesophase. The change in velocity and other parameters [19] at the transition results from disordered molecular arrangement in isotropic phase to an ordered arrangement of molecules in the liquid crystalline phase with long-range orientational order [20]. The variation of adiabatic compressibility [21] is remarkably linear in the isotropic and mesomorphic phases, but it shows a step jump at the isotropic-mesophase transition. The result of molar compressibility varies linearly with temperature at the isotropic phase transition. In this study, the higher values of thermal expansion co-efficient in mesophase than in the isotropic phase confirm the tendency of increasing order of molecule with decrease in temperature. It is firmly established that the ultrasonic velocity and the related parameters [22] are structure dependent. Besides, depending on the structure, they are related to intermolecular interactions and degree of molecular order in liquid crystalline mixture. It is well known that in liquid crystalline phases, the molecules are arranged in order and the orderliness increases from

Iso→Cho, Cho→SmA, SmA→SmC, SmC→ReSmA, ReSmA→SmE and SmE→SmB phases. The induced reentrant smectic-A phase is known to exhibit at different temperature and at different concentrations of the given molecules compared to cholesteric and induced smectic phases such as SmA, SmC, SmE, and SmB phases [23, 24].

Thermodynamic Responses Of Birefringence:-

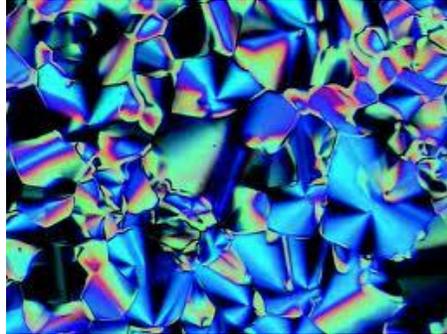
Studies on different mixtures of liquid crystalline materials are more important not only from the viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions [25]. Thermodynamic studies are very important role to understand the phase stability, chemical structure and dynamics of liquid crystals [26, 27]. Temperature dependent molecular orientations of liquid crystalline phases have been considered in many technological applications. The applied applications of these technologies are based on the properties of molecular structure and intermolecular interactions. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive interactions are they individually or together may be responsible for increasing or decreasing the thermal stability of liquid crystalline phase [28]. Thermodynamical variations of liquid crystalline phase at different concentrations of ternary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph thermodynamical responses of variations of birefringence as a function of mole fraction for the sample of CN in LPC+H₃PO₄ at constant temperature 55 °C is presented in Figure 4, which clearly shows, the degree of microphase separations are one of the parameters to controlling a physical properties of liquid crystalline materials [29]. In this context the existence parameter can be varied infinitesimally small either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. The figure clearly illustrates that, statistically how the molecular interactions are thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here we noticed that: at constant temperature the given molecules are fractionally varies as increasing the concentrations of the additive molecules. In this study it is very interesting to observe the spin temperature. Due to the temperature gradients on the molecular surface: the internal degrees of freedom of the molecules are thermodynamically equilibrium with one mole fraction to the other mole fractions. If either increasing or decreasing the mole fraction; which cause a small variation of electrostatic potentials and which they around the molecule. In spite of these uncertainties, the full sets of partial charges are very useful, as it can provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential very well. The molecular density of mesosphere, charges on the given molecules represents an electrostatic molecular interaction, but they do not show the real charge distribution in this molecule. The molecular ordering or the phase stability of liquid crystalline phase at given constant temperature: the intermolecular interactions are responsible for the charges of carbon and the adjacent hydrogen molecules and which shows the correct electrostatic potentials are reproduced by different partial charge distributions.

Conclusions:-

The salient features of this investigation are the following: The existence of cholesteric and induced reentrant smectic-A phases have been observed by using microscopic technique in ternary mixture of CN in LPC+H₃PO₄. The temperature variation of density across the cholesteric and smectic-B are more predominant than the other phase transitions. The anomalous behavior of liquid crystalline physical properties, such as ultrasonic velocity, adiabatic compressibility, and molar compressibility, is discussed at the isotropic mesosphere transition. Thermodynamical response of birefringence have also been discussed to understand: statistically how the birefringence is

thermodynamically changes at different concentrations in order to show the thermal stability, phase stability, chemical structure and molecular dynamics of multi-component system of liquid crystalline phase.

Figure 1:- Microphotographs showing,



a) Focal conic fan shaped texture of SmA phase at temperature (250X).



b) Schlieren texture of SmC phase at temperature (250X).

c)

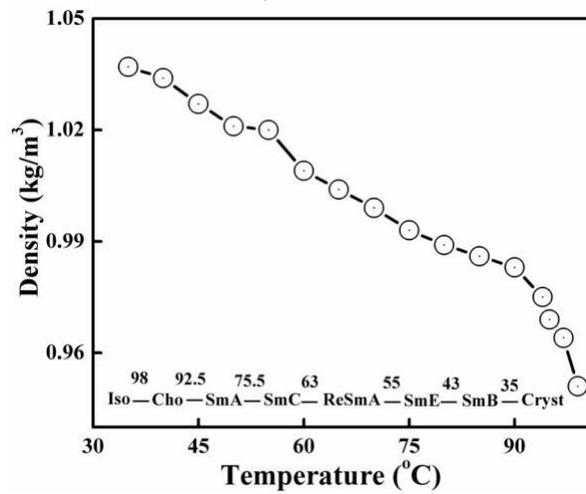


Figure 2:- Temperature variations of density for the sample of 11% CN in LPC+H₃PO₄.

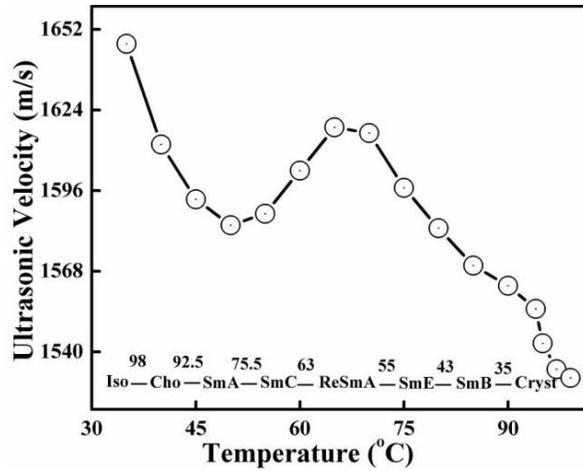


Figure 3(a):-The temperature variation of ultrasonic velocity for the sample of 11% CN in LPC+H₃PO₄.

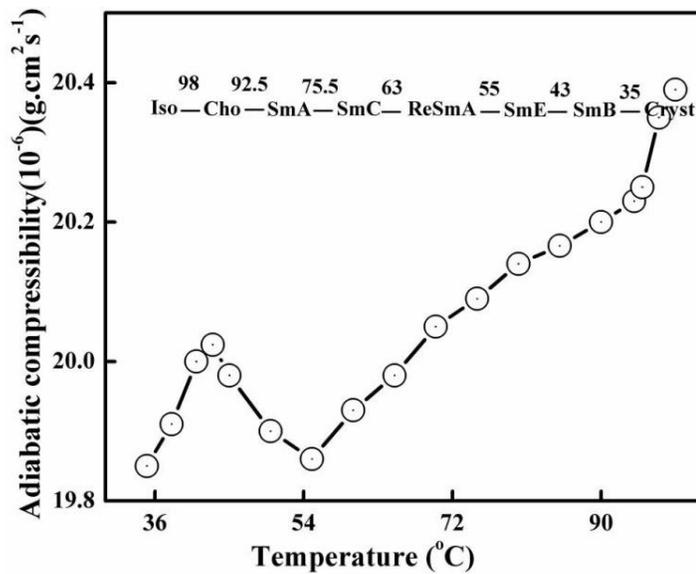


Figure 3(b):- The temperature variation of adiabatic compressibility for the sample of 11% CN in LPC+H₃PO₄.

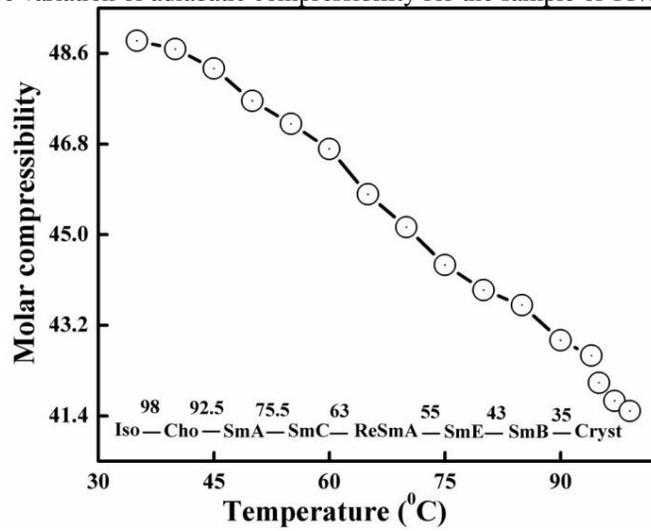


Figure 3(c):- The temperature variation of molar compressibility for the sample of 11% CN in LPC+H₃PO₄.

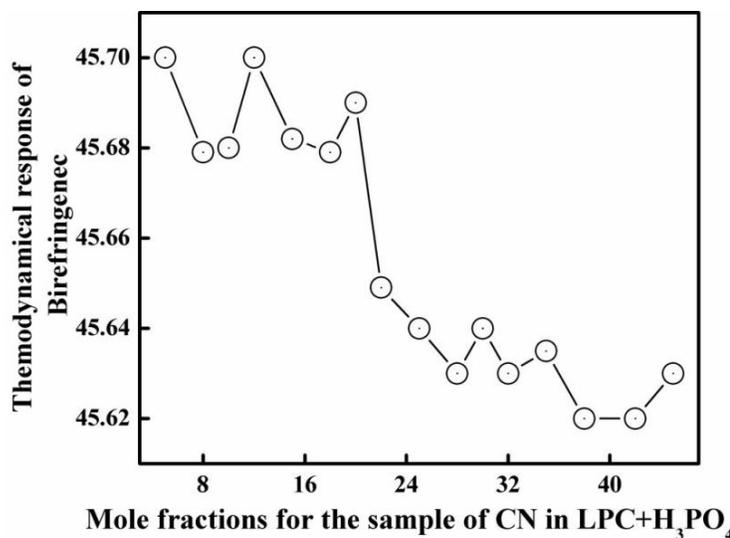


Figure 4:- Variations of thermodynamical response of birefringence as function of mole fractions for the sample of CN in LPC+H₃PO₄.

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