Frontiers in Health Informatics ISSN-Online:2676-7104
www.healthinformaticsjournal.com
2024; Vol 13: Issue 3 Open Access

Variations of Entropy and Thermal Diffusivity Effect on the Morphology of Induced Chiral Smectic Phase of Liquid Crystals

Short running title: Variations of Entropy and Thermal Diffusivity Effect on The Morphology of Induced Chiral Smectic Phase of Liquid Crystals

V. Sivaprasad[1] and T.N. Govindaiah[2]
[1] Department of Physics, Government First Grade College, Channapatna-562160,
Karnataka, India.
[2] Post-Graduate Department of Physics, Government College (Autonomous), Mandya-571401,
Karnataka, India.
Corresponding author: varakuti@gmail.com and tngovi.phy@gmail.com

Cite this paper as: V. Sivaprasad, T.N. Govindaiah (2024) Variations of Entropy and Thermal Diffusivity Effect on the Morphology of Induced Chiral Smectic Phase of Liquid Crystals. *Frontiers in Health Informatics, 13* (3), 8943-8951

ABSTRACT

We report the results of our studies mainly focus on thermal and optical properties of a system comprising the ternary system of organic molecules such as Curcumin, dodecanol and Ortho phosphoric acid. Mixture of these molecules exhibits a very interesting induced SmA-SmC and SmC phases respectively at different temperatures and at different concentrations. In our studies we discuss the estimated values of entropy and thermal diffusivity effect on morphological phase behaviour of liquid crystals towards the isotropic phase transition with the help of conductivity and polarizability data. Wave length dependent refractive indices are helps to study the Sellmeier constants A and B and thermo-optical coefficients have also been discussed.*

Keywords: *Optical studies: Entropy: Thermal diffusivity: Polarizability: Conductivity: Sellmeier equations: Thermo-optical co-efficient:*

Introduction

In recent years the research has mainly focused on the optical anisotropy of liquid crystals: such as wave length dependent refractive indices are an essential parameter for an industrial application of display in various branches of science and technology. In liquid crystalline molecules, average directions of all the segregated molecules are easily re-oriented with respect to external fields such as temperature, electrical field and magnetic field, etc. And hence these are exhibited the anisotropy of its optical, electrical and magnetic properties. Among all anisotropic properties, refractive index of liquid crystal has great importance in the view of device applications. The functioning of the liquid crystal devices utilizes the temperature induced and electric field induced refractive indices [1-5].

In the present paper mainly focuses on optical and thermal properties of ternary components namely: Curcumin, dodecanol and Ortho phosphoric acid. Different concentrations of given molecules show an induced polymorphism of chiral smectic phases respectively at different temperatures and at different concentrations.

Entropy effect and thermal diffusivity of liquid crystalline materials has been discussed. Estimated values of Sellmeier constants A and B, and thermo-optical coefficients have also been discussed.

Experimental Section

In the present work, for our experimental studies, we have considered the ternary mixture of curcumin molecules are at 25% of concentration and 40% concentration of dodecanol in addition with 35% of molecules of orthophospheric acid. To ensure homogeneity: the ratio of given mixtures were kept in desiccators is exposures to many cycles of heating, stirring and centrifuging. The phase transition temperatures of the mixtures were measured using a Gippon-Japan polarizing microscope in conjunction with a hot stage. For microscopic observations: the mixture of given samples were takes on the slide. Refractive indices in the optical region were determined at different temperatures using multi-wavelength Abbe-refractometer (Atago: DR-M4) at λ=486, 546, 589nm. The permitted temperature control was $\pm 0.1^{o}$C. The level of liquid crystal in the capillary was read to ±0.01mm with a cathetometer. The absolute error in the density measurements was $\Delta\rho = \pm\ 0.0001$ g/cc [6-8].

Results and Discussions

Microscopic Observations on Liquid Crystalline Phases

Gippon-Japan-polarizing microscope was used to observe the molecular orientations of optical textures of induced polymorphic phases: they were exhibited by the samples of lyotropic liquid crystals, such as: Curcumin, dodecanol and Ortho phosphoric acid. The exhibited smectic-A, smectic-C and smectic-C* phases shows the formations of induced chiral smectic phases respectively at different temperature. Microscopically observed smectic-A and smectic-C* phases are shown in the Figure 1(a, b). From the figure it has been observed that: the change in morphology causes different phases of liquid crystals, because it influences on thermal variations molecules: Maier and Saupe theory describing a molecular interaction in terms of anisotropic dispersion forces. Dispersion forces and packing factor molecular systems are more important to thermodynamic parameters: such free energy, entropy, enthalpy, etc. The variation of temperature causes the changes in value of entropy towards from isotropic to crystalline region, the molecular reactions are helps to shows the molecular self assembly of induced polymorphic phases. Maier-Saupe theories are also very useful for to explaining how the density of the molecules jump from crystalline to isotropic phases and hence it correlate between thermal stability and anisotropy of molecular polarizability of the induced phases. The anisotropy of molecular orientation and stability of the internal energy of given system are itself in different forms, which are either internal or transient: During these phase transition, the kinetic energies are associated with the structural formation of molecules, which can be released by chemical and atomic reactions. Internal energy of the system depends on the properties of materials, such as composition and physical form, as well as the environmental variables (temperature, pressure, electric field, magnetic field, etc). [9].

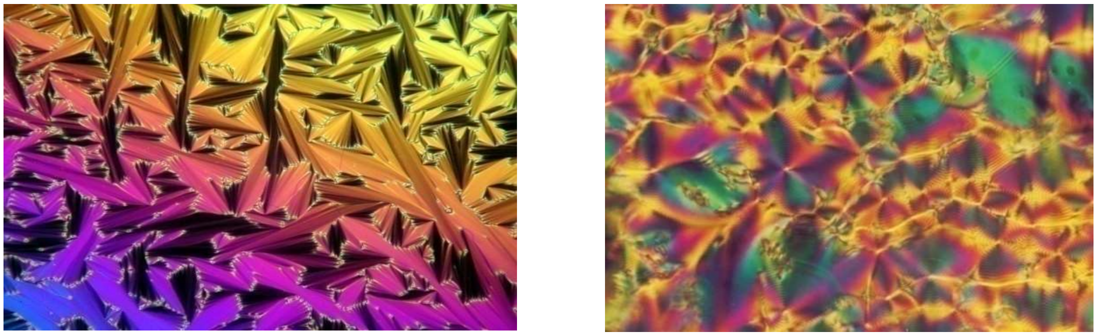

Figure 1: (a) Focal conic fan-shapedtexture of SmA phase.(b) Radial fringes on the fans of focal conic textures of SmC* phase.

Entropy Effect on The Morphology of Liquid Crystalline Phases

Entropy measures the state of randomness or a measure of disorder; it is an important scientific concept, which helps to study the state of disorder or uncertainty. During the phase transition studies: the appearance of increase or decrease of entropy towards the higher/lowers internal energy causes the formation of phases which leads to changes in the randomness or self organizations of molecules, the structural effect on the molecular phases impacts on the overall entropy. The entropy can be determined with using the lattice model. The group of molecules is oriented independently from each other; therefore, the entropy S can be found from the Boltzmann formula

$$S = K_B \ln W$$

where $K_B$is the Boltzmann constant, and W is the number of accessible microstates.

In this study Maier-Saupe theories are helps to describe the interaction of molecules in terms of dispersion forces. Such force shows an inter-molecular interaction related to the packing of molecules and it implies the molecular order and spectral properties that can found from microscopic observation. Temperature variations of entropy are as shown in figure 2. From the figure it clears that: the molecules are randomly disorder with increasing the temperature. As increasing the temperature, entropy can be increased: in which there is energy transport across the system. Either by increasing or decreasing the entropy of the system; which are related to the molecular structure, the degree of molecular activity and physical composition of the system [10-15].

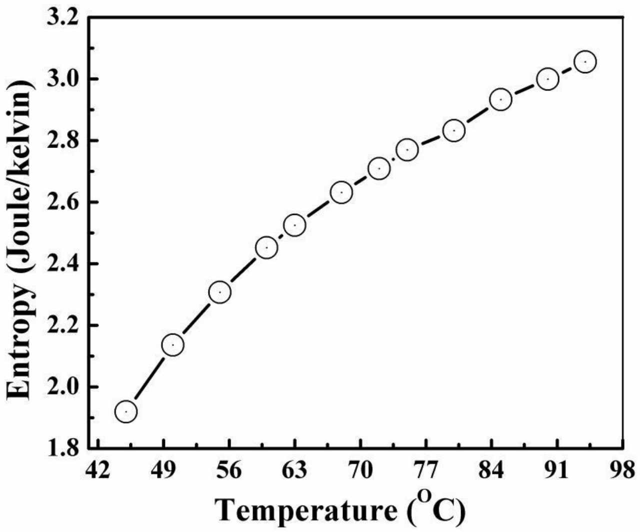

Figure (2). Temperature variations of entropy at different temperature of liquid crystalline mixture.

Studies on microscopic forms of energies are called the internal energy of the system, in which the molecules are randomly distributed as kinetic energy at the molecular and sub molecular levels. At higher temperature, the distribution of kinetic energies of the molecules is more dispersed than that of lower temperature. During phase transition studies: the entropy of any molecules increases with temperature.

Accessible microstates are the liquid crystal phase formations of layer structure can estimate from the theory of dispersion forces. Classical formula for the interaction of molecular energy between one atoms of molecule to the neighbouring molecule: that can explain by using the formula

$$W(r) = \frac{2\hbar\omega\alpha_0^2}{r^6}$$

Here$\hbar = {h}/{2\pi}$, h is Planck's constant. ω is frequency α is molecular polarizability and r is the distance between the atoms of one layer of molecules to other layer of molecules. For the calculations of accessible microstates: variations of temperature are converted in to frequency for the changes in the layer of molecules. Results of this theory: which are applicable to the qualitative agreement with quantum mechanical theory: Landau. Maier-Saupe used this formula for the calculations of accessible microstate of phase formations of molecular disorder parameter.

The changes in entropy of molecules or self organizations of phase formations of layers of molecules leads to molecular polarizability for the appearance of liquid crystal phase become stable. This theory explains the correlation between thermal stability of liquid crystal phase and anisotropy of molecular polarizability [16]. The temperature variations of Accessible microstates of liquid crystalline mixture are as shown in Figure 3. From the figure, it illustrates that: the entropy of layer molecules described as measuring the internal energy of molecular systems are dispersed by a number of accessible microstates in terms of layer of phase formations of molecules, in which there shows the number of different molecular arrangements of its energy at the next instant. On the surface of molecules, the thermal variation of entropy depends on the energy dispersing molecules among in all accessible microstates. An increase in entropy of layer of molecules involves more and more energy dispersion with different microstates of the systems towards final state than in its initial state.

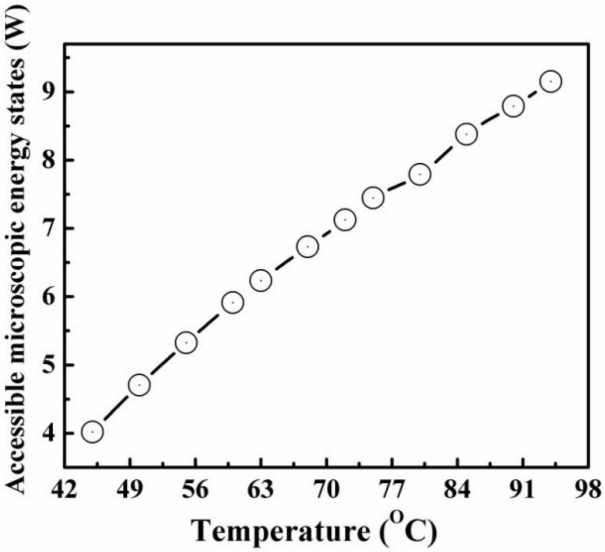

Figure 3.The temperature variations of Accessible microstates of liquid crystalline mixture.

The tendencies of increasing entropy of layer molecules are to fill space and to spread out particle space and energy in all possible ways.

Specific Heat Capacity of Liquid Crystalline Phase

Heat capacity of an object can be calculated dividing the amount of heat energy supplied (E) by the corresponding change in Temperature (T)

$$\boldsymbol{C_p = {E}/{T}}$$

C_p= Heat capacity, E= heat energy, entropy depends on the heat energy. T = change in temperature.

From the system: entropy is a measure of heat transfer of energy in to the system: where as the temperature increases, entropy of the system can also be increases. An increase in temperature causes the increase in kinetic energy of the molecules on the appearance of isotropic to nematic phase transition. Orientations of moving molecules have much more disorder slowly at temperature and hence the heat energy increases the total energy of the system. This gives more kinetic energy distributed among all the molecules of the system.

The temperature variations of heat capacity of liquid crystalline materials are as shown in the following figure 4.

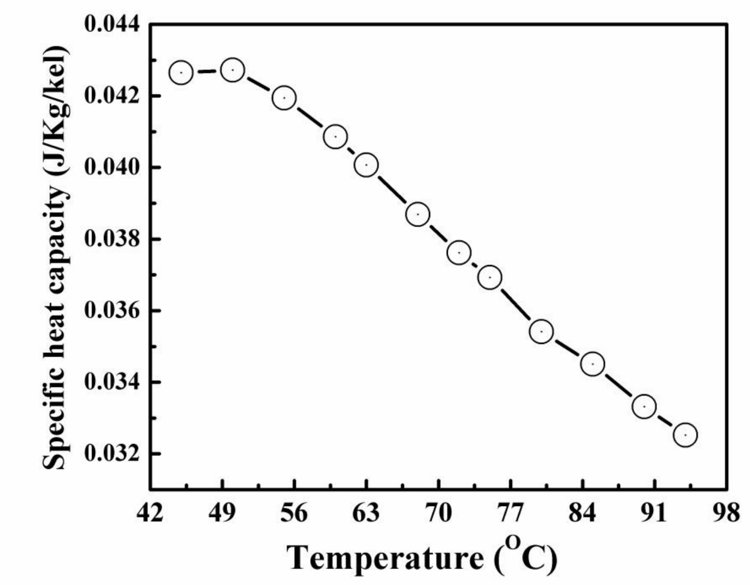

Figure 4. The temperature variations of heat capacity of liquid crystalline mixture.

From the figure it has been observed that: heat capacities of the substances are controlled by a manner in which the internal energy of molecules is distributed among all of its constituent molecules. As the temperature increases, the specific heat capacity of liquid crystalline molecules decreases. Remarkably it is an important to note that: for the given mixture, thermal energy of molecules can vibrate the atomic molecules and hence thermal motion of atomic energy of the molecules is contributes to explain the specific heat of liquid crystalline molecules. Due to the thermal motion: thermotropic and lyotropic molecules, the heat-capacity studies help to provide very useful qualitative information regarding the order of phase transition behaviour from crystalline to isotropic phase transition. This occurs due to the competition between the co-operative atomic (molecular) interaction energy and the entropy of the system. Therefore any phase transition can associate with an exchange of heat to the thermal environment of the system: that balances the changes in the internal free energy [17, 18].

Thermal Diffusivity Studies on Crystalline - Isotropic Phase Transition.

Heat transport mechanisms are the partially ordered matter, Example: liquid crystals are an attractive and important for electro-optic and opto-electronic display device: not only in basic science but also from the technological point of view. Thermal diffusivity of materials shows: diffusion rate of particle can control thermal conductivity in more complex system of liquid crystals. For example: different anisotropic properties of polymers or partially crystallized materials are an important for these applications.

We know that the formula for Thermal diffusivity of material is

$$\boldsymbol{\alpha} = {}^{\boldsymbol{k}}/_{\boldsymbol{\rho}\, \boldsymbol{c_p}}$$

Where α= thermal diffusivity, k is the thermal conductivity, ρ is the density and C_p is the specific heat capacity of the material. Thermal conductivity of polymeric materials is known to be effectively enhanced by the liquid crystalline materials. The property of conductivity of liquid crystalline materials shows a greater magnitude in the orientational direction of molecules in crystalline to isotropic region. Geometrical structural properties of the molecules affecting the orientation order. The temperature variations of thermal diffusivity of liquid crystalline mixtures are as shown in figure (5). From the figure, it illustrates that: at lower and higher temperature, thermal conduction is the diffusion of thermal energy of vibrating atomic molecules within the material. At higher temperature, the vibrating atomic molecule has more kinetic energy: in which there will be an inelalstic or elastic collision occurs between the series of molecular distributions of atomic molecules, kinetic energy of vibrating molecules causes thermal energy throughout the surface [19]. For the critical behavior on the surface of diffusion of vibrating molecules, dips were observed in thermal diffusivity of distributed molecules at at the I-SmA and SmA-SmC- SmC* transitions as well as at the isotropic (Iso)-N transition.

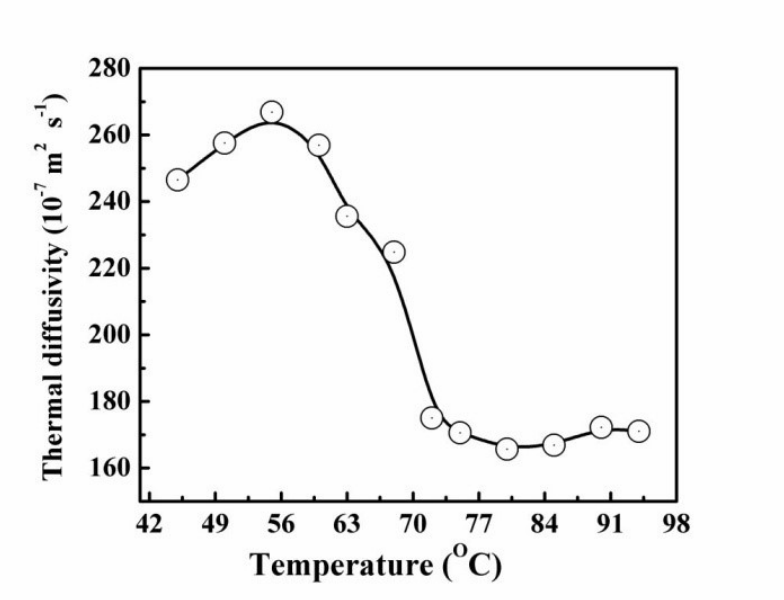

Figure 5. The temperature variations of thermal diffusivity of liquid crystalline mixtures.

Sellmeier Equations on Liquid Crystalline Materials

Sellmeier equation is an equation in the form of mathematical relationship between wavelengths and refractive indices of a material. Temperature-dependent Sellmeier equations are used for various applications of linear and nonlinear optical devices. Sellmeier constants A and B are estimated by choosing the experimentally measured data of refractive indices of optical birefringent materials. Wavelength dependent refractive indices for ordinary and extraordinary waves are approximated in the form of coefficients of Sellmeier equations: and it provides an appearance of signal on the liquid crystal display device. In which they are the function of different optical properties of liquid crystalline molecules. For the set of different wavelength of different colour such as green and blue: the birefringent material describes the Type-1 and 2 phase matching by the different optical properties.

For this study: we consider temperature dependendent multi-wavelength refractive indices of mixture of liquid crystalline materials at different concentrations. Then it is analyzed the Sellmeier constant A and B by using the Sellmeier equation.

For different concentration of liquid crystalline materials, two data sets of refractive indices will be obtained according to temperature dependent multi-wavelength abbe refractometer. We know that: the Sellmeier equation

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - B} \qquad \text{--------------(1)}$$

Where n is the refractive index of the given material. From the Sellmeir equations Sellmeier constants A and B are obtained by using a different wavelength of refractive indices such as λ=486 nm, 546 nm.

$$n_G^2 = 1 + \frac{A\lambda_G^2}{\lambda_G^2 - B} \quad \text{----------}2$$

$$n_B^2 = 1 + \frac{A\lambda_B^2}{\lambda_B^2 - B} \quad \text{---------}3$$

Subtracts the equations 2 and 3, simplified equations gives the Sellmeier constants A and then constant A is substituted to any of equations either 2 or 3; we get the Sellmeier constants B. By the experimentally measured data of wavelength dependent refractive indices are substituted to the corresponding equation; the values of Sellmeier constants A and B are obtained. The following Table shows the refractive indices for the wavelength λ=486 nm, 546 nm and Sellmeier constants A and B.

Temp (^{O} C)	A (10^{-29})	B (10^{-29})
45	7.4151	3.556
48	7.1186	3.558
52	6.4577	3.542
57	6.4326	2.964
61	6.5076	2.793
65	6.2546	2.690
70	6.6718	2.549
74	6.4548	2.480
80	6.6553	2.309
83	6.9385	2.281
86	6.5963	2.197

From the table: it is very clear that: Sellmeier constant A and B values are decreases towards the increasing temperature. The decrease in Sellmeier constants are appear several factors such as changes in refractive indices with temperature and also the optical behavior of the materials across all wavelengths. Sellmeier constant are helps to describe how the liquid crystalline material interacts with light of different wavelengths. By the electromagnetic theory, a beam of light is an electromagnetic wave, in which it concers the atoms or molecules of given matter, in between the bonds: the charges in the material vibrates. Vibrations produced by the frequency due to a resonance event in the material. The different concentration of given material defines changes in the material that stimulate changes in the vibrational frequency of the atomic bonds in the material. Sellmeier coefficients are essential tools for to understanding the different characterization and optical behaviour of organic materials in various applications and hence it allows for the precise control of light in optical systems [20-22].

Thermo-Optical Coefficient Studies On Liquid Crystalline Mixture.

Refractive indices of the optical materials are not a constant parameter over the temperature region, optical materials such as crystal, semiconductors and glasses. These types of materials are used in different optical and photonic systems. The variation of refractive index with temperature at a constant pressure is called the thermo optical coefficient. The analysis of thermo-optical coefficients are key to characterize the temperature dependent non-linear optical devices are semiconductor technology and photonic device. Particularly technological effect is characterized by the thermo-optical coefficient (TOC) and it is related to the behaviour of optical properties of refractive index, when temperature is modified.

From the Lorentz-Lorenz expression, the Prod' home relation can be obtained as:

$$TOC = \frac{(n^2-1)(n^2+2)}{6n}(\phi - \beta)$$

Where T is the temperature, n is the refractive index, and ϕ is the electronic polarizability. Volumetric expansion coefficient β is defined as:

$$\beta = \frac{1}{\rho}\frac{d\rho}{dT}$$

where ρ is material density. Due to the affinity of quantum dot liquid crystal display technology, chromonic phases of liquid crystalline molecules are of particular interest in integrated to thermo-optical devices. However, the photo emissive quantum dot particles of the devices are presently high fabrication costs, as well as low electrical power consumption. The present studies are helpful to maintain the temperature of these properties. Furthermore, due to its low thermo-optic coefficient; the efficiency of refractive indices in chromonic phase of liquid crystals are exhibited by the molecules is more than 10 times lower than that for polymers. The thermo-optical co-efficient are as shown in Figure 6. Liquid crystalline mixture with low melting point, the thermal expansion is very small. As increasing temperature, thermo-optical coefficients are also increases at some certain saturation point and also it is dominated by the volume change in polarizability. The thermo-optical coefficient in liquid crystals is a crucial parameter: that describes how the refractive indices of liquid crystal material changes with temperature. The thermo-optical coefficient is essential for controlling the optical properties of the liquid crystal layers within a liquid crystal display, ensuring that the display functions are correct across a range of operating temperatures.

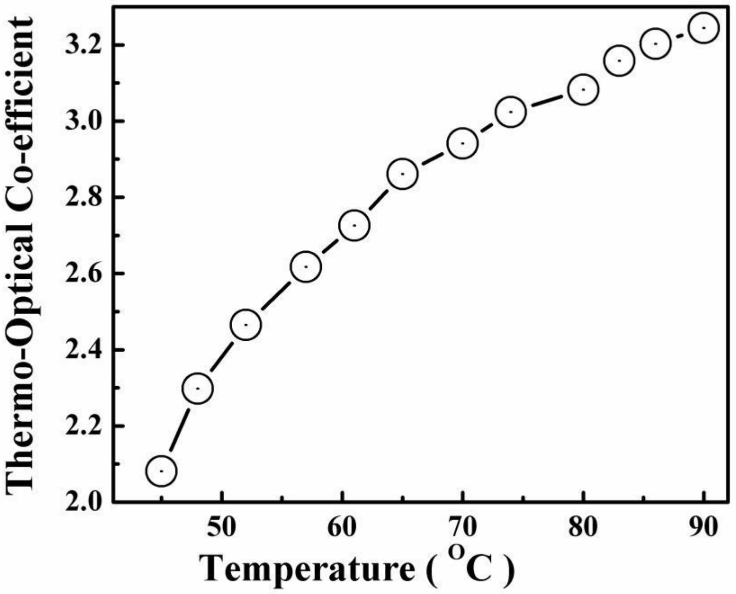

Figure 6: The temperature variations of thermo-optical co-efficient of liquid crystalline mixtures.

High thermo-optical coefficients are used in thermo-chromic devices, such as temperature-sensitive labels and thermometers. These materials change colour or optical properties with temperature, making them useful for temperature monitoring and displays [23-27].

Conclusion

Optical microscopic investigations of ternary mixtures of long chain organic molecules show the existence of induced chiral mesomorphic phases such as SmA-SmC and SmC* for given concentrations respectively at different temperatures. The experimentally measured data of density, wavelength dependent refractive indices and conductivity measurement are used to estimate the values of entropy, thermal diffusivity and thermo-optical coefficient of liquid crystalline materials. The studies are helps us to understand the morphology of induced chiral smectic phases and also impact on the order of phase transitions of different phases respectively at different temperature during the transition from crystalline to isotropic phase transition. Sellmeier equations are helps to describe how the liquid crystalline material interacts with light of different wavelengths and its optical behaviour used in various applications for controlling the wavelength of light in optical systems.

REFERENCES

[1].Neto, A.M.F.and Salinas, S.R.A. 2005.The Physics of Lyotropic Liquid Crystals: Phase Transitions and Structural Properties; Oxford University Press: New York, NY. USA.
[2].Petrov, A.G. 1999. The Lyotropic State of Matter: Molecular Physics and Living Matter Physics. Taylor & Francis: London.UK.
[3].Reinitzer, F. and Beiträge zur Kenntniss des Cholesterins. 1888. Monatsh. Chem. 9. 421–441.
[4].Virchow, R. and Myelinformen. Arch. Pathol. Anatom. 1854. Physiol. Klin. Med. 6. 572.
[5].Ghosh, G. 1997. Applied Optics. 36(7): 1540-6.
[6].Marthandappa, M.and Nagappa. 1992. Phys. Stat. Sold (a). 129, 389.
[7].Nagappa, Revanasiddaiah, D. and Krishnamurti D.1983. Mol. Cryst. Liq. Cryst. 101,103-127.
[8].Govindaiah, T. N. and H. R. Sreepad. 2015. Mol. Cryst. Liq. Cryst. 616, 1–6.
[9].Demus, D. and Richter, C. 1978. Textures of Liquid Crystals, Weinheim: New York, NY.
[10].Dadivanyan, A. K., Chausov, D. N., Belyaev, V. V. and Academician A. S. Bugaev. 2014. Doklady Physics. 59(10). 457–459
[11].Maier, W. and Saupe, A.1960. Naturjorsch. 158, 287
[12].Chickos, J. S. and Acree, Jr. W. E. 2003. Thermochim. Acta 395, 59.
[13].Chickos, J. S. and Acree, Jr. W. E. and Liebman, J. F.1999. J. Phys. Chem. Ref. Data 28, 1535.
[14].Maier, W. and Saupe, A., 1959. Naturjorsch. 14a, 882
[15].Straley, J. P. 1976. Phys. Rev. A 14, 1835.
[16]. Kamala latha, B. and Sastry, V. S. S. 2018. Mol. Cryst. Liq. Cryst., 45(13-15). 2197–2213.
[17].Chandrasekhara, S. and Madhusudana, N. V. 1970. Mol. Cryst. Liq. Cryst. 10, 151–171.
[18].Shin, S. T., Satyendra Kumar, and Finotello, D. 1992. Phy Rev A. 45(12), 8683
[19].Suleyman Yilmaz and Ahmet Yildirim. 2019. Int J Thermophys.30, 2015–2020.
[20].Ghosh G 1997 Applied Optics. 36(7), 1540-6
[21].Bodurov, I., Vlaeva, I., Marudova, M., Yovcheva, T., Nikolova, K., Eftimov, T. and Plachkova, V. 2013. J. Bulgarian. Chem. Communi. 45, 81.
[22].Misto, Endhah Purwandari, Supriyadi, Artoto Arkundato, Lutfi Rohman, and Bowo Eko Cahyono. 2021. Journal of Physics: Conference Series.1825, 012030.
[23].Nishihara, H., Haruna, M. and Suhara, T. 1989. Optical Integrated Circuits,McGraw-Hill Book Company, New York.
[24].Born, M. and Wolf, E. Principles of Optics, 6th Edition. Cambridge University Press, Cambridge, UK (1997).
[25] Prod' homme, L.1960. Phys. Chem. Glasses 4, 119-122.
[26] Govindaiah T. N.. Mol. Cryst. Liq. Cryst. 625. 99-105. 2016.
[27] Govindaiah T. N.. Mol. Cyst. Liq. Cryst. 633. 100-109. 2016.