Thermal and Dielectric behaviour of nematic EPAP Valerate mesogen

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***Abstract*— Polarizing optical microscopic studies reveal that the EPAP Valerate is having single phase variant nematic and it is also enantiotropy. The low frequency static dielectric constant and microwave frequency, dielectric permittivity increased with the increase of the concentration of the solute in non-polar solvent benzene at room temperature. The optical refractive index value decreased with the increase of the concen-tration of the solute in a non polar solvent benzene at room temperature. Dipole moment value obtained from the dilute solution method is sufficient to determine the dipole moment in liquid crystal phase.**

***Keywords*— EPAP Valerate , dielectric constant, refractive index, dipole moment, liquid crystal.**

I.INTRODUCTION

Liquid Crystals (LC) represent systems of fascinating materials, which are widely recognized for their applications in display devices [1-4]. They are classified as to belong to an important phase of matter that is attached [5] with both scientific and technological importance. Materials in LC phase exhibit boh [6] the fluid and crystaline properties in such a manner to utilise them in many applications and modern appliances [7] like thermography, electro-optical (EO) displays, medical diagnostic tools. LC phases are a state of matter that carries the resemblances [8] of both anisotropic crystal and isotropic liquid. This phase of matter was discovered [9] in 1888 by an Australian Botanist Reintzer, and later named [10] as Liquid Crystals by Lehmann. Although LC retains the properties of liquid upto certain extent, it exhibits the anisotropy (pertinent to crystals) prevalently, when it is cooled down. This dual nature has resulted to cause profound influence on the physical properties in all phases. Hence, its response is expected to be of resulting [11] a subtle and complex nature to the external stimulus (viz., electrical, magnetic, mechanical, optical, thermal etc fields). Owing to particular combination of flow and anisotropy aspects, the behaviour of LCs renders to be interesting as well as readily usable [12, 13] in flat display panels. It is noticed that a material exhibits liquid crystallinity, if it is fixed in certain geometrical and configurational constraints with respect to its molecular structure and design. By increasing the temperature, a crystal melts and the centres of mass of molecules (which were earlier located on a 3-dimensional periodic lattice) are disturbed to some extent. The change in symmetry of the structure is observed through the change of sharpness in X-ray diffraction peaks, which gets diffused as to indicate the inducement of some sort of short range order (among the centers of mass of the molecules). These observations strongly suggest that, there is some sort of positional order that prevails over the long range orientational order of molecules in the LC state [14-16]. However, both of these orders disappear to a large extent by heating the substance in to the liquid state. Some solids are known to change the polarization state of the emergent light, which liquids do not so [17, 18].

II. EXPERIMENTAL

To identify the different phases and to determine transition temperatures a polarizing microscope, OLYMPUS BX50 (serial number 56512, made in Japan) with computer controlled Instec (USA) temperature controller hot stage is used. To photograph the textures the polarizing microscope is provided with a DP 10 camera attachment. Accuracy of temperature measurement is ± 0.1 ^{o}C. The refractive index of a liquid can be measured using Abbe type refractometer. The instrument used was supplied by ASCO AS-17760. The low frequency static dielectric constant (1 kHz) is measured by using Digital LCR meter (PLCR-8C) supplied by Pacific Electronics (PVT) Ltd.

Preparation of samples:

EPAP Valerate was supplied by M/s Eastman Organics, USA. Benzene was supplied by M/s Qualigens and it is ExcelaR grade and was double distilled before use. Benzene is used as solvent, and EPAP Valerate is used as the solute in the preparation of solution. EPAP Valerate is dissolved in benzene in various concentrations, the various weights of EPAP Valerate for each concentration for 25.0 ml (volume of plunger) of benzene. All the weights are measured using a single pan electronic balance Dhona make, model 100 DS with an accuracy of 0.01 mg

Table1: Weight of EPAP valerate in benzene

Mole fraction of EPAP Valerate in benzene	Weight ofEPAP Valerate (grams)
0.02 %	1.78132
0.03 %	3.63686
0.04 %	5.57137
0.05 %	7.58998

III. RESULTS AND DISCUSSIONS

Polarising Microscopic Study:

The compound EPAP Valerate, which belongs to the azo compounds family [19], exhibits a single phase variant in between solid crystal and isotropic phase. The observed phase is enantiotropic. In heating cycle the EPAP Valerate exhibits nematic[20] phase in between the temperatures 77.1^{o}C and 125^{o}C. On further heating the nematic phase becomes isotropic above 125^{o} C. In cooling cycle, the nematic phase appears at 125.5 ^{o}C and this phase is up to 76.9 ^{o}C. On further cooling it becomes as solid below 76.9 ^{o}C . In heating and cooling cycles nematic droplets are observed. The transition temperature corresponding to EPAP Valerate given by M/s Frinton Laboratories, Inc., USA [21] is also given in Table 2. Sharma reported [22] on their laboratory prepared compound, the nematic phase appears in between 78 ^{o}C and 126 ^{o}C. The values are depicted in Table1. For further confirmation of the phase, miscibility studies [23] are also carried out. The compound EPAP Valerate is mixed with EPAP Hexanoate which also exhibits phase variant nematic. This phase of EPAP Valerate is co-miscible with the phase of EPAP Hexanoate. This confirms that the identified phase of EPAP Valerate is nematic and it is enantiotropic.

Table:2 Phase transition temperatures

Study	Crystal to Nematic	Nematic to Isotropic
Present [H]	77.1 ^{o}C	125 ^{o}C
Present[C]	76.9 ^{o}C	125.5 ^{o}C
Frinton Labs [3]	78 ^{o}C	126 ^{o}C
P.B.K.Sharma[4]	78 ^{o}C	126 ^{o}C

Dielectric constant:

The different concentrations of EPAP Valerate solute system is dissolved in non-polar solvent benzene at various volume concentrations. The dielectric constant of each concentration is measured at optical frequency, low frequency 1 kHz and microwave frequency 10 GHz at room temperature. The dielectric constant in the optical region is obtained by measuring refractive index using the Abbe refractometer with a sodium D light (wavelength 5983 A^{o}) as a source. The low frequency static dielectric constant (1 kHz) is measured by using the LCR meter and the complex dielectric constant (ε^{*}=ε'-jε") in the X band (8-12 GHz) microwave frequency region is measured by using the waveguide plunger method [24] and cavity perturbation technique [25]. The dielectric data at microwave frequency for different concentrations of the solute EPAP Valerate are given in Table 3.

Table 3.Comprehensive data on dielectric constant at different frequencies

% of EPAP Valerate in benzene	ε_{static}	$\varepsilon_{microwave}$ (plunger technique)	$\varepsilon_{microwave}$ (cavity technique)	$\varepsilon_{microwave}$	n^2 (Optical frequency)
0.02%	2.35	2.31-j0.02	2.37 - j0.04	2.31-j0.02	2.28
0.04%	2.50	2.35-j0.07	2.44 - j0.09	2.35-j0.07	2.26
0.06%	2.64	2.52-j0.11	2.55 - j0.13	2.52-j0.11	2.25
0.08%	2.71	2.57-j0.14	2.57 - j0.16	2.57-j0.14	2.23

Table 4: Comprehensive data on dielectric constant, relaxation time, dipole moment for various concentrations of EPAP Valerate in Benzene

% of EPAP Valerate in benzene	ε_{static}	$\varepsilon_{microwave}$ (plunger)	n^2 (Optical frequency)	Relaxation Time τ (pico sec)	Dipole Moment μ (Debye)
0.02%	2.35	2.31-j0.02	2.28	30.9	2.18
0.04%	2.50	2.35-j0.07	2.26	26.0	
0.06%	2.64	2.52-j0.11	2.25	7.6	
0.08%	2.71	2.57-j0.14	2.23	7.3	

Relaxation time:

In order to calculate the relaxation times, Abbe refractometer for measurement of high frequency dielectric constant using the refractive index, LCR meter for static dielectric constant and the plunger method in microwave frequency region was used to evaluate the dielectric data. All these data were used to fit in an Argand diagram (ε' Vs ε'') to calculate the relaxation times. It is observed that a distribution of relaxation times as witnessed from Cole-Cole arc plot instead of Debye arc plot.

The corresponding parameters obtained from Cole-Cole arcs such as distribution parameter 'α' and the corresponding angle $\theta = \pi\alpha/2$ and also the corresponding u, v parameters are given in Table5 along with the corresponding relaxation times.

Table 5: Data on u, v, θ, α and relaxation time

EPAP Valerate in benzene	U	v	θ	Distibution parameter(α)	Relaxation time (pico sec)
0.02%	0.8	1.2	35	0.3888	30.9
0.04%	2.4	3.3	32	0.3555	26.08
0.06%	5.4	3.5	28	0.3111	7.6
0.08%	7.2	4.1	24	0.2666	7.38

Conclusion:

It is evident from the data given in the Table 3, the dielectric constant increases with the increased frequency. The microwave data show that these compounds are polar in nature and correspondingly the dielectric constant is a complex quantity. The relaxation time is found to decrease in magnitude for a given concentration of EPAP Valerate in benzene with the increase of dilution in benzene. However from the present study the dipole moment is obtained 2.18.From the above results, it is observed that with the increase of frequency dielectric constant is decreasing at room temperature and also for any concentration. The reason is obvious and the contributions from the polarizations are decreasing with the increase of frequency and it is observed that the optical refractive index value decreased with increase in the concentration of the solute EPAP Valerate in a non polar solvent benzene at room temperature which shows that the angle of refraction may be increasing.The microwave and low frequency static dielectric constants increased with the increase in the concentration of the solute in a non-polar solvent benzene at room temperature which shows that the dielectric constant of the solute EPAP Valerate is higher and also polar in nature.There is a decrease in the relaxation time as the concentration of the EPAP Valerate is increased in non-polar solvent benzene which reflects that the strength of dipole is increasing.

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