Effect of Bridging Group on the Dielectric Properties of Liquid Crystal

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Abstract—Several factors influence the dielectric properties of liquid crystal materials. The value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors. In addition, the types of molecular arrangements in a liquid crystal phase and the thermodynamic conditions are also important. In order to investigate which factors are dominating, the dielectric properties of substances that belong to one homologous series have been studied. We find that for sample, the values of dielectric parameters depend on the rotation of molecule and inter-layer permeation of layers producing a correlation between cores in adjacent layers. We have accounted for dielectric properties and how these properties are influencing the dielectric parameters. The phase transition temperature agrees the transition temperature determined by DSC study. For our liquid crystal material, the dielectric properties are significantly influenced by the bridging group, polar groups and many more - now question arises how these parameters affect dielectric factors has been discussed in the paper in detail.

Index Terms—Liquid crystals, Dielectric constant, Activation analysis, Thermal analysis

I. INTRODUCTION

Liquid crystals are the materials that already have enriched our understanding of the condensed state of matter in many ways and promise a wealth of future applications. They have, so far, primarily been applied in electro-optics because they combine anisotropic properties such as optical birefringence (previously thought to be unique to solids), with the property of being soft, but now from technological point of view its applications are going on increasing [1-6]. We have focused on dielectric spectroscopy. The dielectric spectroscopy method is very well suited to study the rotational dynamics of molecules in liquid crystalline phases if the constituting molecules posses a dipole moment [7-9]. In the case of liquid crystal molecules, two main relaxation processes can be distinguished: one is connected with the rotations around the short axes and occurs at few hertz frequencies (the low-frequency, LF, process), and the second one is connected with the much faster rotations around the long axes (the high –frequency, HF, process). Such motions are otherwise referred to as molecular “tumbling” and “spinning”, respectively. Of course, both processes can be observed when non-zero projections of the dipole moment on the principal inertia moment axes occur. Besides, the internal motions of polar groups can also contribute to the relaxation spectra [10-12].

Quantitative knowledge of orientational ordering in liquid crystal is necessary for the development of improved materials for application. Thus, attempts are being continuously made to study the material properties for the better insight into the basic understanding of the liquid crystalline behavior [13, 14].

Several factors influence the dielectric properties of liquid crystal materials. The value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors. In the addition, the types of molecular arrangements in a liquid crystal phase and the thermodynamic conditions are also important. In order to investigate which factors are dominating, the dielectric properties of substances that belong to one homologous series or those having slightly different structures, should be studied [15].

Dielectric studies provide useful information about molecular structure, molecular dynamics, phase transition and display performance of liquid crystals. Most of the dielectric studies on liquid crystals are concentrated in the nematic phase and usually examine the nematic -Isotropic phase transition. The optical characteristics, threshold voltages and switching times of liquid crystals are strongly dependent on the absolute value of their dielectric permittivity. Dielectric relaxation studies provide one of the few techniques for finding the nature of molecular reorientation within a system. Dielectric studies of a large number of thermotropic liquid crystalline substances have been conducted and thus dielectric spectroscopy is found to be one of the best techniques for measuring dielectric permittivity and dielectric losses with high accuracy and sensitivity. Most applications of liquid crystals depend upon the possibilities of changing orientation of the liquid crystal molecules by the applied electric fields, which in turn depends on the visco-elastic and electrical properties of such materials [16-18].

In the present paper we have investigated the dielectric,
thermal properties of mesogen exhibiting Smectic A (SmA) phase.

II. EXPERIMENTAL DETAILS

A. Material
The sample under investigation is liquid crystal molecule: (E)-4-chloro-N-(2-((2-((E)-(4-chlorophenyl)imino)methyl)-5-(octadecyloxy)phenoxy)(oxo)vanadio)oxy)-4-octadecybenzylidene)aniline (say CCMA) exhibits SmA mesophase. This molecular assembly can be of extreme importance, because widened temperature range. Figure shows the molecular shape of the CCMA- from which it can be noticed that the molecule is neither rod-like nor disc-like. The phase transition scheme along with its 3D structure given below.

![Chemical structure](image)

**Fig. 1.** Chemical structure with its transition scheme

B. Preparation of cell
Two similar cells having active area 25 mm², (sheet resistance and the visible light transmission are 10Ω/mm² and more than 90%, respectively) were prepared by using transparent and highly conducting ITO (Indium Tin Oxide) -coated (Diamond Coating UK), optically flat glass substrates used as electrodes. These electrodes provide a base to align the liquid crystal sample. To achieve a planar alignment, the electrodes were treated with a polymeric adhesion promoter (Nylon 6/6; Sigma Aldrich) and then rubbed unidirectional with a velvet cloth. The thickness of the cell was maintained at 5 µm by means of Mylar spacers (Liquid Crystals Technologies, USA). The cells have been calibrated using standard AR grade liquids like benzene (C₆H₆) and carbon tetrachloride (CCl₄). The material was introduced into the cell by capillary action at a temperature 100°C above the isotropic temperature of the sample. Alignment of the sample was confirmed by placing the sample into crossed position of polarizing microscope CENSICO (7626). The correct and proper alignment of the liquid crystal molecules is extremely important for precise measurements of electrical properties and which, in turn, influences dielectric parameters [17, 18]. Correct alignment plays an extremely important role in determining molecular geometry. Thus, uniform alignment and pretilt angle control for a liquid crystal on solid-substrate surfaces is also very important from application point of view.

C. Dielectric permittivity
The dielectric behavior of the material has been studied in the frequency range 100Hz-10MHz by using a computer- controlled impedance/gain phase analyzer Hewlett Packard (HP 4194 A). The dielectric parameters were measured as a function of temperature and frequency. In order to vary the temperature a microprocessor-based heating device (Julabo – F25) has been used. The experiment was performed at very slow heating rate, and temperature was measured and controlled with accuracy of ±0.01°C. The sample was left for 10 min before starting the measurement at a particular temperature of the sample. Dielectric parameters are very sensitive to impurities and so experiments have been performed in dust free atmosphere for accurate measurements.

D. Thermal studies
A Differential scanning Calorimeter (DSC) scan was performed by a power compensated calorimeter (NETSCHZ) [19] controlled by a computer.

RESULT AND DISCUSSION
We have determined the different dielectric parameters of the sample using the Cole-Cole dispersion equation [20] given by

$$\varepsilon^* = \varepsilon'_\infty + \frac{\delta \varepsilon'}{1 + (j\omega\tau)^{1-\alpha}}$$

(1)

Here $\delta \varepsilon'$ is the dielectric strength of the material, $\varepsilon'_\infty$ is the high frequency limit of the dielectric permittivity, $\omega$ (=2πf) is the angular frequency, $\tau$ is the relaxation time and $\alpha$ is the distribution parameter. If the value of $\alpha$ is small and approaches zero, the above equation will satisfy the Debye type of relaxation phenomena, but for values more than 0.5, the above equation suggests the existence of more than one relaxation process.

The sample cell geometry introduces errors in the data in both the low and high ends of the frequency range investigated. Therefore, the experimental results required a low- and high- frequency correction. On separating real and imaginary parts of the equation (1) and adding high- and low- frequency correction parameters, we find:-

$$\varepsilon' = \varepsilon'_\infty f^{-\alpha} + \varepsilon'_\alpha + \frac{\delta \varepsilon'[1 + (2\pi f \tau)^{1-\alpha} \sin(\alpha \pi / 2)]}{1 + (2\pi f \tau)^{2(1-\alpha)} + 2(2\pi f \tau)^{1-\alpha} \sin(\alpha \pi / 2)}$$

(2)

and
bridged by an electronegative oxygen atom is observed to respond rather slowly to the external field in this type of relaxation resulting in exhibiting such a trend.

Illustration of dielectric permittivity with frequency figure 4 (a). Initially, at lower frequency the trend is represented as shown in figure, and this is maintained due to “tumbling” motion - which can be co-related with slight molecular rotation around the short molecular axis (LF process) such motion are referred to as molecular “tumbling” where as when frequency is increased in SmA phase the same constant trend is observed but this time such motions are referred to as spinning. This constancy in trend has been obtained due to the bridging group attached in the molecule, which plays a vital role in maintaining constancy at higher and lower frequencies shown by Schematic representation of the dielectric dispersions in liquid crystals (a) reorientations of entire molecules around their short axis (b) reorientations of entire molecules around their long axis and (c) intermolecular reorientations of bridging group. Thus two different phenomenon’s (LF and HF process) maintain a balance in the system due to intermolecular reorientations of bridging group (figure 4 (b)). As, bridging group in the central core part of the liquid crystal moiety is more rigidly fixed in the molecular structure than the end chains ,which are relatively free to rotate. Thus, the bridging group in the present liquid crystal sample is so attached that it gradually maintains a balance at LF and HF giving constrains to the slight motions.

\[
\varepsilon'' = \frac{\sigma_{dc}}{\varepsilon_0} + \frac{\delta \varepsilon'(f \tau)^{(\mu - \alpha)}}{1 + (2\pi f \tau)^{(\mu - \alpha)}} - 2(\pi f \tau)^{(\mu - \alpha)} \sin(\alpha \pi/2) + Af^m
\]  

Where \( \sigma_{dc} \) is the ionic conductance, \( \varepsilon_0 \) is the free space permittivity and \( f \) is the frequency, while \( n, m \) and \( k \) are the fitting parameters. The terms \( \varepsilon_{dc}, f^\alpha \) and \( \sigma_{dc}/\varepsilon_02\pi f^\alpha \) are added in equations (2) and (3) to correct for electrode polarization, capacitance, and ionic conductance at low frequencies. The term \( Af^m \) is added in equation (3) for high frequencies to correct for the ITO sheet resistance and lead inductance of the cell. By a least square fitting of the above equations using experimental data, we have removed the low and high frequency errors.

Cole-Cole plot of the sample, while it is in the SmA phase, has been drawn at specific temperature 101°C as shown in figure 2. In the figure, black squares represent experimental data while solid red line shows best theoretical fitting of the Cole-Cole equation with the data. Using such plots, values of dielectric parameters, such as the relaxation frequency and dielectric strength, have been evaluated.

The relaxation studies provide information about the molecular reorientation of the molecules. Figure 3(a) shows the variation in relaxation frequency with temperature. Sample exhibits SmA phase and the relaxation peak gradually increases with increasing temperature, indicating that such situations (increase in temperature) may produce a distortion in the molecular shape, but with further increase in temperature layered smectic structure is maintained, infact with further increase in temperature- the strict adherence of the molecules in the layered form is weakened due to increased thermal vibrations, which is caused by the intramolecular reorientations of polar sites as represented in figure 3(b) , actually nitrogen atom has five electron in their outermost orbit in which three are involved as a bonding electron (as a single bond with phenylene ring ), rest two are as lone pair of electron , since venedium(V) is transition metal which shows variable valency (means require electron to complete the octate (acc. to octate rule) that’s why a co- ordinate are formed with N atom (because nitrogen atom have lone pair of electron) in our structure which is denoted by aero, thus this N and V interaction is responsible for this type of trend which results in re-orientation of the longitudinal dipole moment pertaining to the flexible end chain...
which directly affects the dielectric permittivity [bridging groups for our sample could be defined as -Two separate rod like liquid crystal molecules species 1 and species 2 are connected with V (vanadium), N and O acting as spacer between the two rod like combinations and so these interactions are resulting in such behavior ] and so such a trend has been established by the liquid crystal sample.

Relaxation strength of the sample is represented in figure 6, increases on increasing in temperature. As smectic phase exhibit molecular tilt and in our case their occurs fluctuations in the orientation of the long axis of the individual molecules which are not equally probable in all directions around the director, this tends to alter the layer spacing causing non-cylindrical symmetry about the director which is also influenced by the structure of molecule in our case and so such a trend is observed.

The Arrhenius equation describes the behavior for a process from one state to another separated by a potential barrier (Such as for example a double wall potential) and the height of the barrier translate the activation energy. In liquid crystal devices the relaxation time is of extreme importance which depends on the cell gap, the degree of molecular alignment and many other parameters. When a high voltage is applied to the sample cell it affects relaxation time and all these properties depend on the activation energy, which plays a crucial role in many applications. Therefore activation energy has been calculated by using Arrhenius plot of the relaxation time figure 7.

\[
\tau = \tau_0 \exp\left(\frac{W_b}{kT}\right)
\]

Where \(W_b\) is the activation energy, \(k\) is Boltzmann’s constant and \(\tau\) is the relaxation time. The activation energy for this sample is 3.3 meV in SmA phase.

Dielectric loss with frequency has been shown in figure 8. The loss of the sample is due to zig - zag shape of molecule.
which may result in the rotational freezing of the molecule resulting in slight tilting of the molecule at higher temperatures. In our case, bridging group links the terminal chains to the core units in series, and addition of oxygen atom tends to bend the terminal chains away from the long axis of the central part of the molecule. Thus the molecule exhibits the zig-zag picture. Zig-zag molecules can pack tightly into layers, but only if parts of the molecules are tilted relative to a line perpendicular to the layers, and thus the results are in good agreement as observed with other liquid crystals.

![Fig. 8 Variation in dielectric loss with temperature for CCMA](image_url)

The output of a power compensated DSC plots the power difference versus temperature figure 9. One curious aspect of the thermo grams is that the freezing point of a sample is often much lower than its melting point. The difference between these two transition temperatures is often inversely correlated with the time rate of change of temperature at which the transition is approached. These superheating and super cooling effects are inherent characteristics of all materials which posses a first order transition. The heat capacity at constant pressure of the sample is given by

$$C_p = (dH / dT)_p = (dQ / dT)_p = (dQ / dT)(dT / dt)^{-1} = P_d (dT / dt)^{-1}$$  \hspace{1cm} (5)$$

Where (dT/dt) is the temperature scanning rate which is constant and Pd is the power difference (noted on the thermo gram) which varies with temperature.

The heat capacity was calculated before and after transition by modifying equation (5) and writing in the form

$$C_p = \alpha \gamma + \beta \gamma T$$  \hspace{1cm} (6)$$

Where T is temperature and the constant $\gamma$ is 6.0 sec/K. Power is taken to be linearly related to temperature, and $\alpha$ (in mcal/sec) is the intercept on a plot of power versus temperature for a given phase, and $\beta$ (in mcal/K sec) is the slope. For the solid phase just before the transition, the value of $\alpha$ is 0.048 mcal/sec, while the value for $\beta$ is 6.67x10-5 mcal/K/sec. In the liquid crystal phase, that is, after transition, the values of $\alpha$ and $\beta$ change to 0.051 mcal/sec, 6.6x10-6 mcal/K/sec respectively. Thus, with these constants and for any given temperature, the heat capacity can be calculated by using equation (6).

![Fig. 9 DSC plot for CCMA](image_url)

### III. CONCLUSIONS

Several factors influence the dielectric properties of liquid crystal materials. The value and the position of the dipole moment in the molecule, the ratio of the longitudinal to transverse dimensions of molecules, the lengths and flexibility of the terminal groups and the rigidity or an internal rotational freedom in the molecular cores seem to be the most important structural factors. In addition, the types of molecular arrangements in a liquid crystal phase and the thermodynamic conditions are also important. In order to investigate which factors are dominating; the dielectric properties of substances that belong to one homologous series have been studied. We find that for sample, the values of dielectric parameters depend on the rotation of molecule and inter-layer permeation of layers producing a correlation between cores in adjacent layers. We have accounted for dielectric properties and how these properties are influencing the dielectric parameters. The phase transition temperature agrees the transition temperature determined by DSC study. For our material, the dielectric properties are greatly influenced by the bridging group, polar sites.

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