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The analysis of phase transition temperatures of SmA liquid crystal by dielectric characterization

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Due to determining true phase transition temperatures for technological device applications of liquid crystals becomes important. The differential scanning calorimetry (DSC) technique and polarizing microscope (PM) measurement methods are frequently used methods for better understanding of the phase transition temperatures in LCs. We have also researched the dielectric parameters of the liquid crystal in detail. In this study, as an alternative method, phase transition temperatures and dielectric parameters of liquid crystal which exhibits enantiotropic SmA mesophase have been analyzed by means of dielectric spectroscopy measurements. The dielectric parameters of liquid crystal have been calculated by the capacitance method via Impedance Analyzer within the frequency range of 100Hz-10MHz. In order to analyze phase transition temperatures of the LC, the temperature dependences of the real and imaginary parts of the dielectric constant of LC have been calculated. In this way, the influence of temperatures on the dielectric properties of LC and how the dielectric properties change depending on the LC phase within the temperature interval of 25-118 ^{o}C have been revealed. The transition temperatures of LC have been verified by the dielectric measurements by drawing graphics in three dimensions. Dielectric relaxation mechanism of LC has been analyzed by Cole-Cole curves. These curves have been exhibited semicircle and straight line. Vertical lines in Cole-Cole plot is accepted as a super-capacitive behavior.

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1. Introduction

Liquid crystals (LC) are intermediate states between crystals and isotropic liquids. Liquids can flow, for example, while solids cannot, and crystalline solids possess special symmetry properties that liquids lack. Ordinary solids melt into ordinary liquids as the temperature increases. Some solids melt twice or more as temperature rises. Between the crystalline solid at low temperatures and the ordinary liquid state at high temperatures lies an intermediate state, the liquid crystal [1]. In other words, Liquid crystals (LCs) are form intermediate phases, the so-called mesophases, which are located thermodynamically between a crystalline solid and an isotropic liquid. Those mesophases differ from each other in their degree of order and symmetry. For thermotropic LCs, two of the most common mesophases are the nematic (N) and the smectic A (Sm A) phases, both of which demonstrate a long-range orientational order. In the N phase, the molecules tend to orient along the same direction, the so-called director, while in the Sm A phase, without any long-range positional order, they are additionally organized in layers so that the director is orthogonal to the layer plane [2 -3]. There are a lot of the types of smectic phases, the most important ones are Smectic A, Smectic B and Smectic C. In Smectic A, the molecules are on the average perpendicular to the layers and their axes have the same orientation [4-5]. LCs have been well documented to have long served as versatile model systems in statistical mechanics. Up to date, several experimental methods, each of which is sensitive to some characteristic property of LC, have been carried out to study the numerous types of phase transitions [6-7]. By these methods, the first-order or second order (continuous) character of the phase transition in particular and the universality class and the related critical exponents of the transition has been widely investigated. Among various phase transitions in thermotropic LCs, the N−SmA transition has been one of the most frequently studied and is still subject to debate [3, 7-9].Over the past decade, there exists an immense interest on the development of liquid crystalline nano composites obtained by dispersing several types of nano structures to LCs. Among these nano structures, owing to their importance from both applicational and fundamental standpoints, nanoparticles (NPs) are of a vast deal of attention due to that LCs have been reported to turn out to be excellent hosts for NPs to modify /improve the electro-optical and viscoelastic properties extremely [10-11].

Liquid crystals (LC) have both mobility of liquids and anisotropy of crystals. These two properties enable liquid crystals to be in used in technological applications [12-17]. Liquid crystals are one of the leading topics in today due to their usage in wide range technological applications such as LCDs, OLEDs, charge carrier materials and optical sensors [18]. Liquid crystal phases are useful in displays because they interact with light and electric fields like crystals, but they can flow like liquids, making it possible to use electric fields to change their effect on light new designs and synthesized molecules in liquid crystal field have a great interest more and more by both academic society and applied scientists [18]. Timeline of the history of liquid crystal phase applications, from their discovery to the present day has been shown in Fig. 1 [19].

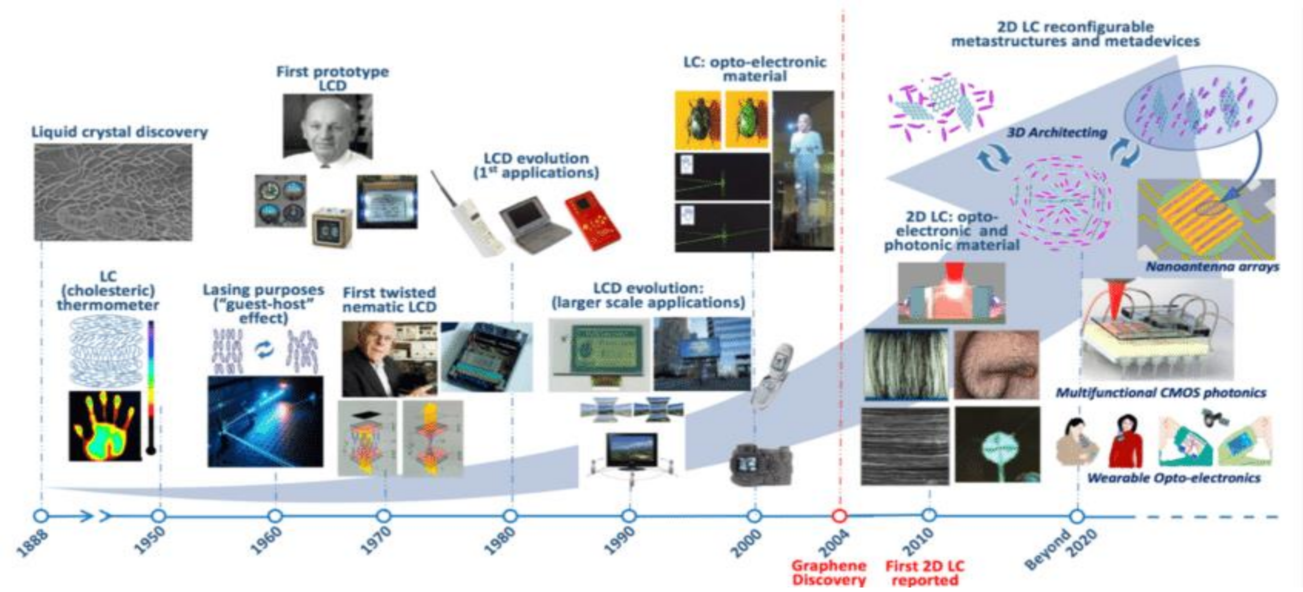


Fig. 1. Timeline of liquid crystal phase applications [19].

The phase behavior of the system is defined by stating the number, qualitative nature, and composition of phases present at equilibrium. The differential scanning calorimetry (DSC) technique provides extensive phase information because it allows one to determine phase boundaries and the extent of heterogeneous regions, to discover three-phase transitions, and to localize invariant points [20]. Differential scanning calorimetry (DSC) also provides the information related to the phase transition temperatures and associated enthalpy and entropy of phase transitions. The confirmation of the phase transition temperatures and characterization of phases by the appearance of optical textures are carried out using polarizing optical microscopy (POM). Vibrational spectroscopic techniques viz. Fourier transform infrared (FTIR) and Raman spectroscopy became powerful tools to study the phase transition in the LCs [21-28].

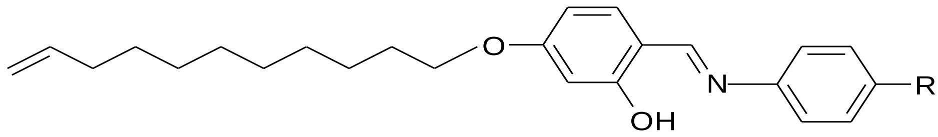
Experimental studies showed that the behavior of liquid crystals (LCs) can substantially change under the influence of electric and magnetic fields. These particular LC properties allowed to make good use of them in practical applications. Most devices including LCs (mainly displays) are based on different types of electro-optical effects [29-31].

Dielectric relaxation spectroscopy has proven to be a powerful technique to study the dipolar ordering and molecular dynamics of collective and non-collective molecular processes in chiral smectic liquid crystals possessing paraelectric, ferroelectric and ant ferroelectric phases [32-35]. In this study, phase transition temperature and electronic properties of liquid crystals, which exhibits enantiotropic SmA mesophase as high temperature phase in a wide temperature range, have been analyzed by means of Dielectric Spectroscopy measurements. The complete characterization of these properties requires the use of variety techniques. Besides, the importance of Differential Scanning Calorimetry (DSC) and Polarizing Microscope (PM) on determining of the phase transition temperatures of liquid crystals, the benefits of Dielectric Spectroscopy (DS) as a useful method was presented in this work.

2. Experimental

2.1. Mesomorphic properties of LC

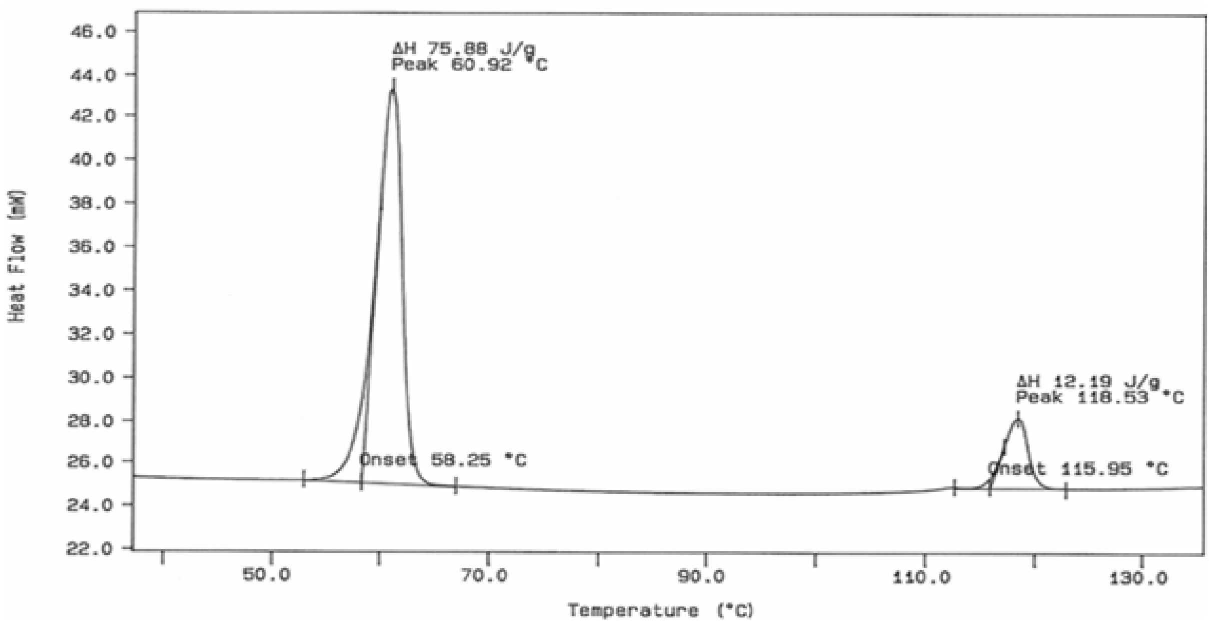
The salicylaldimine compound LC was prepared in usual way [36] The spectroscopic data for LC compound is given in Ref. [37]. The chemical structure, transition temperatures, corresponding enthalpy values have been given in Fig. 2. The temperatures of phase transitions taking place in the LC enthalpies of these transitions were determined by Differential Scanning Calorimeter (DSC). Differential Scanning Calorimetry experimental data of **LC** was taken by Perkin-Elmer DSC-7. The related DSC traces of **LC** compound has been given in Fig. 3. The mesomorphic properties of the LC compound has been studied by polarizing microscopy (PM) technique using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope. This LC exhibits liquid crystalline properties and shows thermotropic enantiotropic mesophase (SmA). Polarizing microscope photographs of **LC** have been given in Fig. 4.



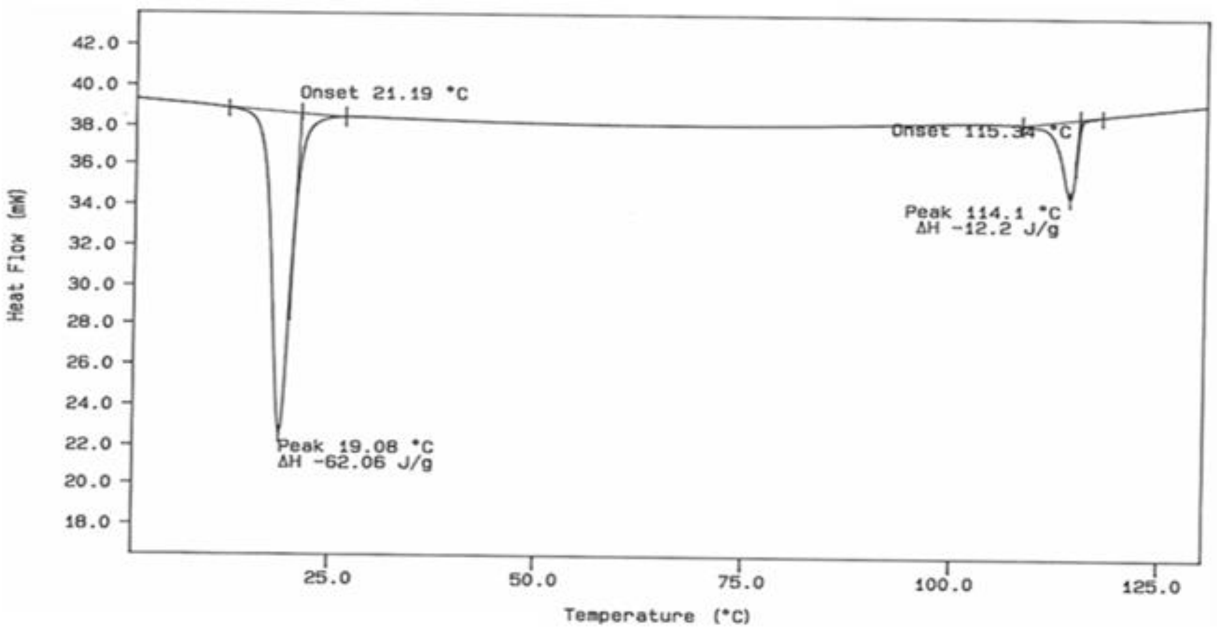
Compound	T/°C [ΔH kJ/mol][a]
LC, R:OC_6H_{13}	Heating ➡ **Cr 60.9 [75.88] SmA 118.5 [12.19] Iso** **Cr 19.08 [-12.2] SmA [-62.06] 114.1 Iso** ⬅ Cooling

[a]Perkin-Elmer DSC-6; enthalpy values in italics in brackets taken from the 2nd heating and cooling scans at a rate of 10 °C min^{-1}; Abbreviations: Cr = crystalline, SmA = smectic A mesophase, Iso = isotropic liquid phase.

*Fig. 2. Phase transition temperatures and transition entalpies of compound **LC***



(a)



(b)

Fig. 3. DSC thermograms of LC on heating (a) and cooling (b)

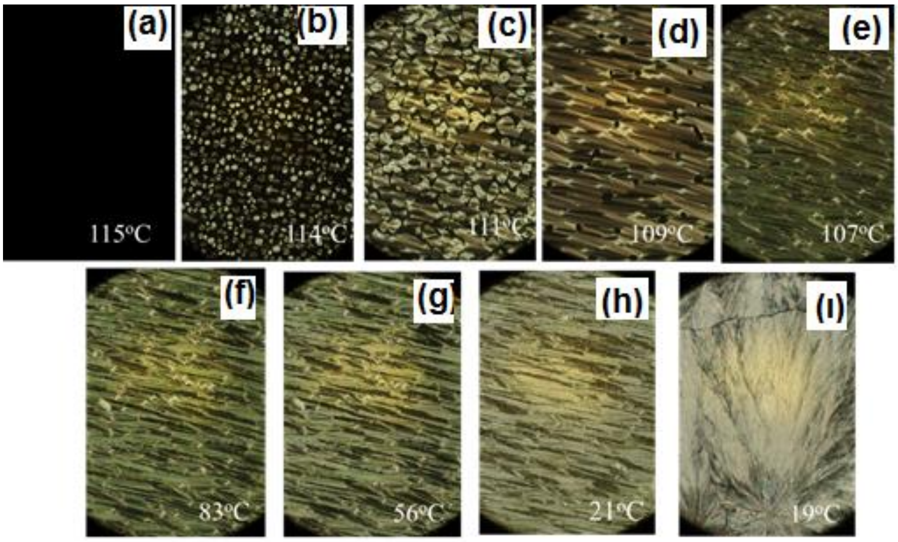


Fig. 4. Polarized light optical photomicrographs of the LC as observed on cooling different temperatures (a) Isotropic phase (b), (c), (d), transition from ısotropic phase to SmA phase (e), (f), (g), (h) SmA phase (ı) Crystal phase (color online)

2.2. Dielectric properties of the liquid crystals

Dielectric Spectroscopy is a useful method and plays an important role in determining the molecular dynamics, relaxation mechanism and phase transition temperatures in liquid crystal systems. In the literature, the dielectric properties of many kind of liquid crystal compounds have been studied in detail [38, 39].

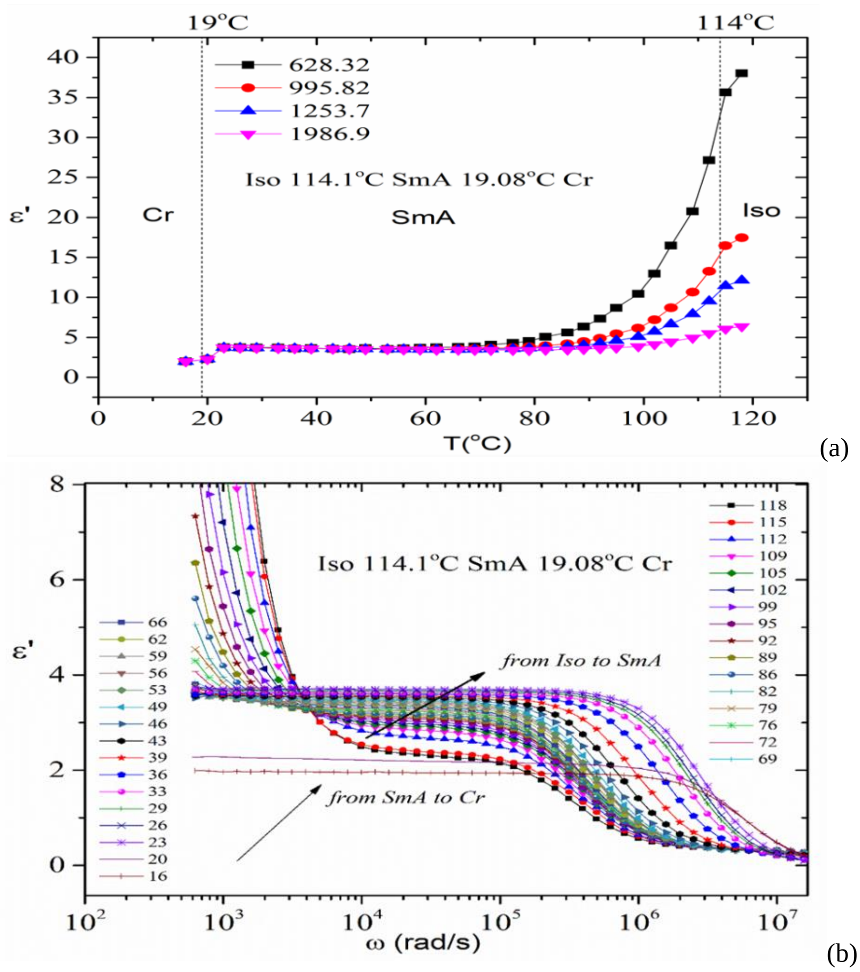


*Fig. 5. The real component of the dielectric constant for LC (a) by temperatures at the selected angular frequency and **(b)** by the angular frequency at different temperatures (color online)*

In the temperature range of study, the real part of dielectric constant curves by the angular frequency can be seen in Fig. 5. It is obvious that, with increasing frequency, the real part of the dielectric constant decreases (Fig. 5a). The electric constant increases sharply after 114 ^{0}C which is the isotropic phase transition temperature (see Fig.5b). The imaginary component of dielectric constant for **LC** by angular frequency at different temperatures has also been shown in Fig. 6.

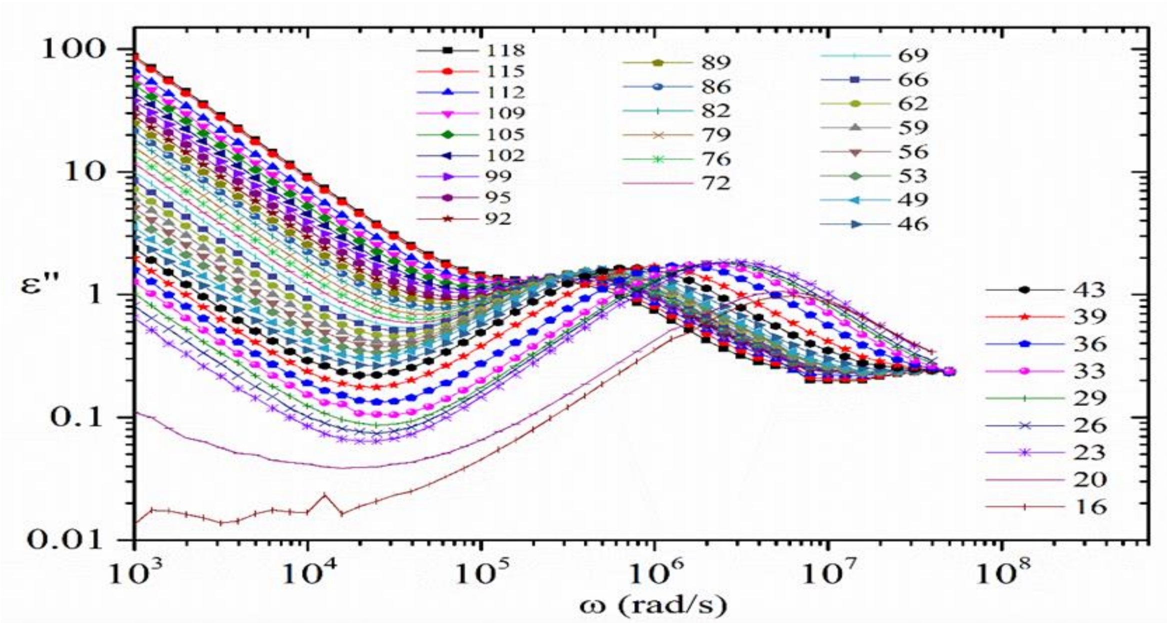


Fig. 6. The imaginer component of the dielectric constant for LC by the angular frequency at different temperatures (color online)

The dielectric parameters of liquid crystal have been calculated by the capacitance method via Impedance Analyzer within the frequency range of 100Hz-10MHz within temperature interval of 16-118 ^{0}C. In order to analyze dielectric relaxation mechanism of the liquid crystals, we have plotted Cole-Cole graphics (Fig. 7). The Cole-Cole plot ($\varepsilon'' vs\ \varepsilon'$) is a powerful tool for materials retaining one or more well separated relaxation processes with comparable magnitudes and obeying the Cole-Cole formalism. The plot comprises of variation of dielectric loss with dielectric storage component at constant temperature and formation of perfect semicircle (after SmA phase transition) indicates the presence of single relaxation time.

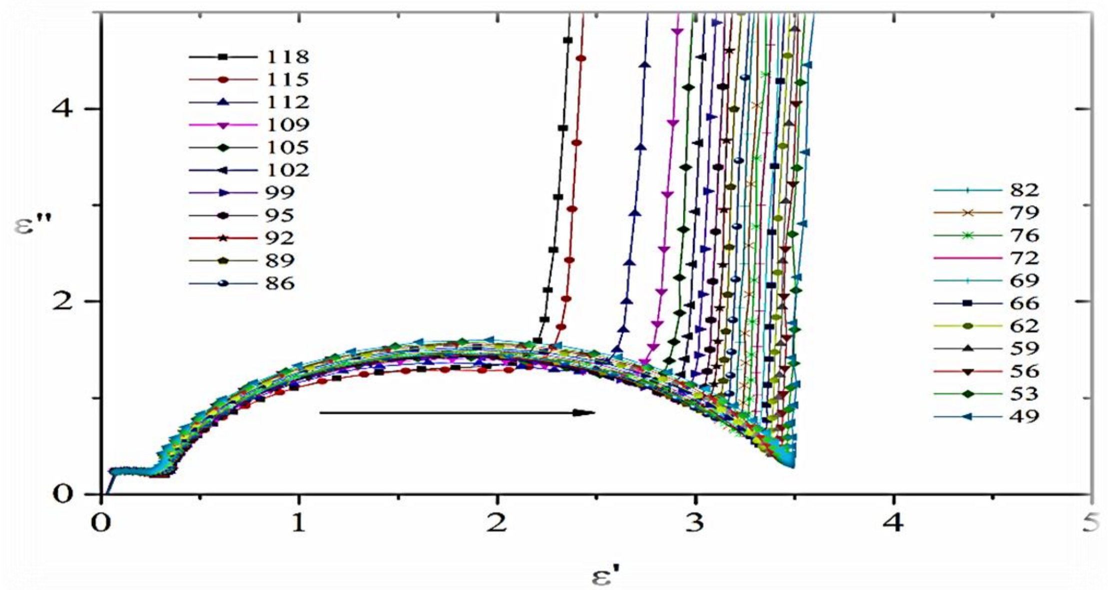


*Fig. 7. Cole-Cole plot of **LC** at different temperatures (color online)*

Three-dimension plots of the complex dielectric permittivity real ε′ and imaginary part ε″ versus angular frequency and temperature for this liquid crystal have also drawn in Fig. 8 and Fig. 9 respectively. The phase transition temperatures for this liquid crystal also can be determined from these graphs.

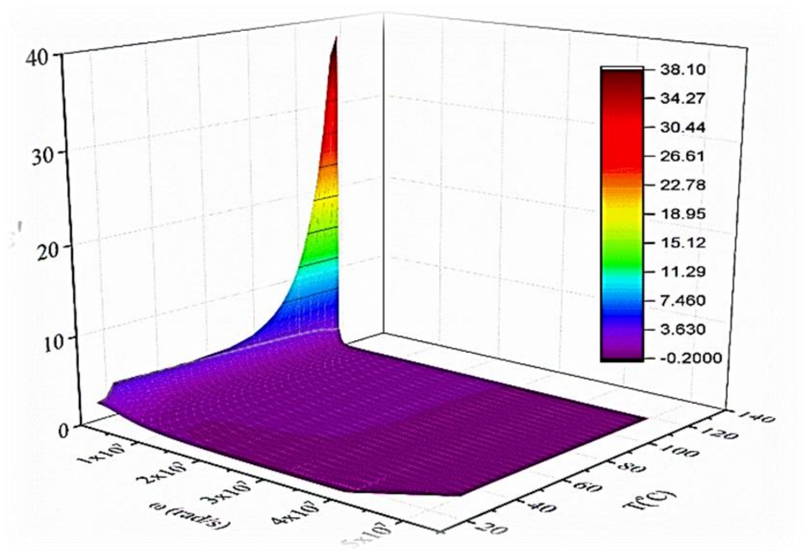


Fig. 8. The typical 3D plot of the complex dielectric permittivity real ε′ versus angular frequency and temperature for LC (color online)

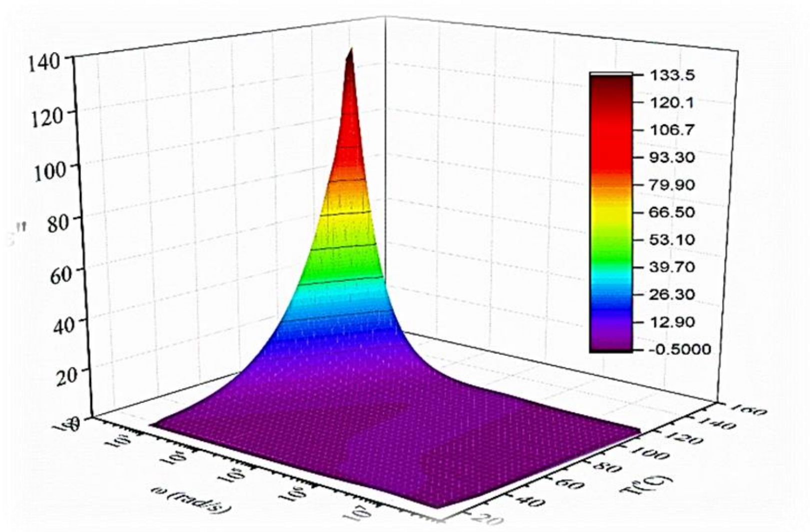


Fig. 9. The typical 3D plot of the complex dielectric permittivity imaginer ε″ versus angular frequency and temperature for LC (color online)

3. Conclusions

In this study, mesomorphic properties have been investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and dielectric properties have been investigated by dielectric spectroscopy (DS) method. This calamitic liquid crystal showed SmA mesophase enantiotropically. Dielectric relaxation mechanism of **LC** has been analyzed by Cole-Cole curves which exhibit semicircle and straight line in SmA phase. Vertical lines in Cole-Cole plot is accepted as a super-capacitive behavior according to publications in literature. Thus, this **LC** can be used in technological applications as super capacitors.

Three-dimension plots of the complex dielectric permittivity real ε′ and imaginary part ε″ versus angular frequency and temperature for this liquid crystal have drawn. The phase transition temperatures for this liquid crystal also can be determined from these graphs. According to impedance spectroscopy results, all dielectric parameters of this LC have been changed in phase transition temperatures. Therefore, the dielectric spectroscopy method may be an alternative method to the DSC and PM method.

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