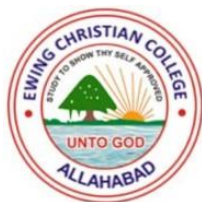


Dielectric properties of Liquid Crystals

Project report



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Last but not least I would like to thank my parents who helped me financially and encouraged me throughout the completion of the project.

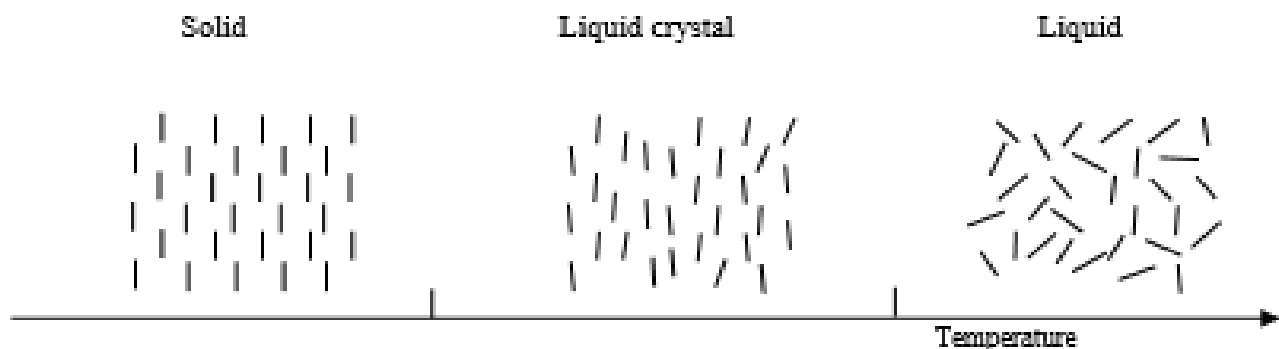
INTRODUCTION

LIQUID CRYSTALS –

The difference between crystal and liquid, the two most common condensed matter phases, is that the molecules in a crystal are ordered whereas in a liquid they are not. The order in a crystal is usually both positional and orientational, in that the molecules are constrained both to occupy specific sites in the lattice and to point their molecular axes in a particular direction. Interestingly enough, many phases with more order than present in liquid but less order than the typical of crystal also exist in nature. These phases are grouped together and called **LIQUID CRYSTALS**.

The molecules in a liquid crystal phase diffuse about much like molecules of a liquid, but as they do so they maintain some degree of orientational order and sometimes some positional order also. The amount of order in a liquid crystal is quite small relative to a crystal. There is only a slight tendency for the molecules to point more in one direction than others or to spend more time in various positions than others. The fact that most of the order of a crystal is lost when it transforms to a liquid.

- It is the intermediate or the interdisciplinary state between the solid and liquid where as the molecules are free to move but are oriented in a particular manner. The molecules have no positional order but retain some orientational order.
- Liquid crystal phase is also called meso phase and the molecules, which can exist in the mesophase, are called Mesogens



Liquid crystals are most widely used in display devices. By the end of the 20th century, the market size of liquid crystal displays (LCDs) alone grew above \$20B and is now replacing conventional cathode-ray tubes (CRTs) with better options. Twisted nematic (TN) liquid-crystal display¹ was reported in 1971 and it found application in watches and calculators as low-information-content LCDs. TN displays are not suitable for high-information-content displays as their contrast ratio is low and the viewing angle narrows when driven at a high multiplexing ratio. Around 1985 a prototype super-twisted nematic (STN) display was demonstrated.^{2,3} STN displays have a steep electro-optical response, and can be used for high-information displays. However, the STN viewing angle is worse than the TN viewing angle and contrast is no better. The only reason for using STN is its higher multiplexability.

in passive matrices. Active thin-film transistors TFTs employ TN. STN displays are now used in mobile telephones, personal digital assistants PDAs, and word processors. However, the response speed of STN LCDs is low, and unsuitable for video applications. They have several disadvantages in resolution, multiplexing level, response time, color, and viewing angle as well. In 1975, Meyer et al. reported ferroelectricity in the chiral SmC SmC* phase of liquid crystals.^{4,5} With the discovery of ferroelectric liquid-crystals FLCs, it seemed that the search of the appropriate material for video application is over when technical application of FLCs was suggested by Clark and Lagerwall.⁶ Ferroelectric LCDs seem to be the most promising LCD due to their extremely fast switching speed and capability for high level of multiplexing. The problems of STN LCDs have been removed in ferroelectric LCDs FLCs to a large extent with improved switching time 0.1 ms and bistability, but not completely. There are several problems in the commercialization of FLCs. Some of them are the small cell spacing 1–2 μm , the problem of the mechanical shock due to unstable molecular anchoring at the surface, and above all the desired gray scale can only be achieved by indirect methods such as spatial or temporal dithering. Recently antiferroelectric liquid-crystal materials have been proposed as prospective material for use in display devices AFLCDs.^{7–13} The antiferroelectric liquid crystals AFLCs are attractive for their tristate switching behavior, easy dc compensation, microsecond response, hemispherical viewing angle in-plane switching geometry, intrinsic analog gray-scale capability, and no-ghost effect. AFLCDs are still in the stage of development and further studies are needed for mass-scale applications. Studies of antiferroelectric liquid crystals are important not only from the application point of view but also from the point of view of basic studies as AFLC materials are showing submesophases such as SmC^{*}, SmC* with the existence of second order transitions. In the present work we are reporting the electro-optical and frequency-dependent dielectric studies of a multicomponent AFLC mixture namely, W-132A showing a wide temperature range SmCA^{*} phase around room temperature 0–48°C.

CLASSIFICATION OF LIQUID CRYSTALS

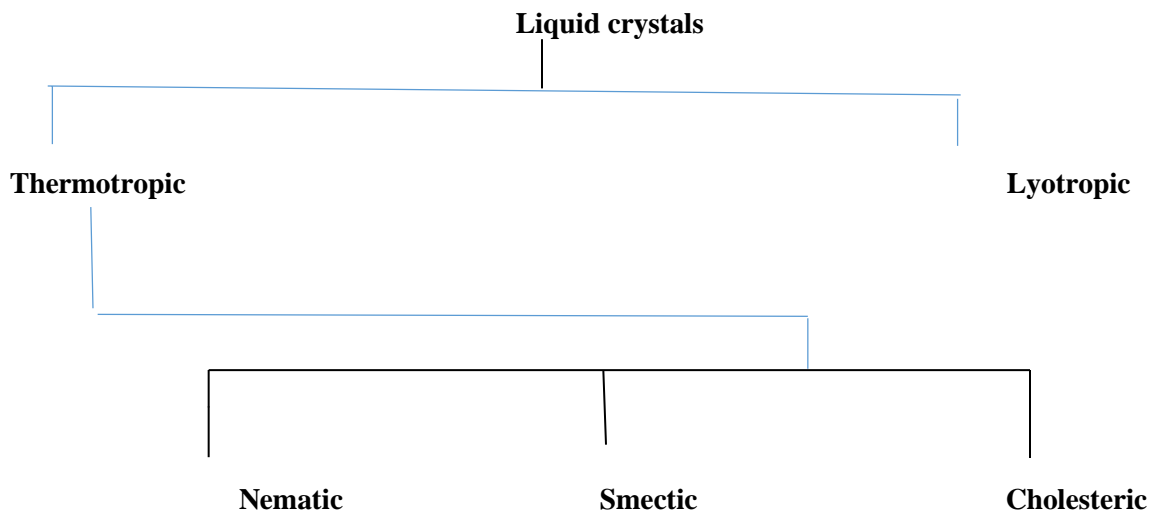
Liquid crystals can be broadly classified into two categories

- **Thermotropic liquid crystal:** Those liquid crystal which exhibit liquid crystalline state on change of temperature alone. This type of liquid crystal depends on the temperature and the thermotropic behavior of the sample. Example–para-Azoxyanisole etc.
- **Lyotropic liquid crystal :** These exhibit liquid crystalline state in mixture and when the concentration of one of the constituents is varied .Example–Soap.

A number of different types of molecules form liquid crystal phases what they all have in common is that they are anisotropic . Either their shape is such that one molecular axis is very different from the other two or in some cases, the interaction between these anisotropic molecules promote orientational and some time positional order in another fluid phase.

The two most common type of molecule that form liquid crystals phases is a rod shaped molecule such compound are called **Calamatic** liquid crystal and many different phases are possible likewise those crystals which have the disc like shape are called the **Discotic** liquid crystal.

Thus liquid crystal can be classified as follows



NEMATIC LIQUID CRYSTALS :-

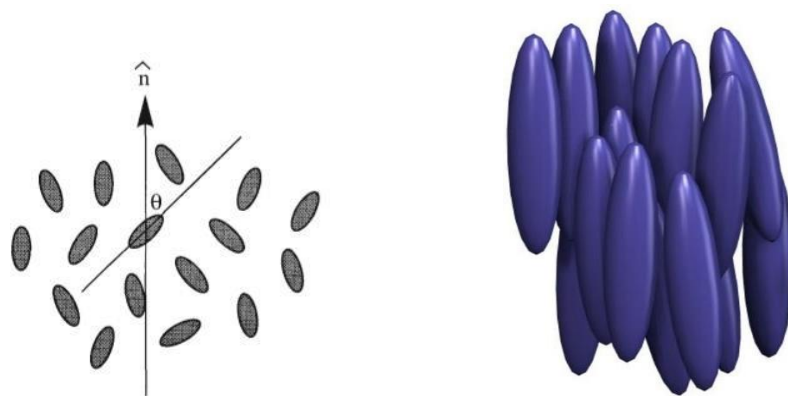
Nematic is a Greek word for thread like structure being so named because its optical texture appeared as a series of optically extinct thread (defect) on a coloured background . A nematic liquid crystal phase can be discovered from both calamatic and discotic molecule.

In a Nematic meso phase molecule possess a long range orientational order with molecular long axes aligned along a preferred direction. There is no long range order in position of centers of mass of molecules. The preferred direction may vary throughout the medium and is called a Director. The orientation of the director is represented by a unit vector $\hat{n}(\mathbf{r})$. (as shown in the figure below) Nematic molecule are able to rotate around their long axes and there is no preferential arrangement of their end even if they differ.

Nematic Liquid Crystal at a glance.

- They have thread like structure.
- Formed from optically inactive compounds.
- Do not have any positional order but the molecules are arranged parallel to one another means they have orientational order.
- Less viscous as they are closely arranged .and fluidity is more .

Example: Cyanobiphenyls



Molecular order in Nematic liquid crystal.

SMECTIC LIQUID CRYSTALS :-

The name Smectic comes from the Greek word for soap, since the mechanical properties of these phases reminded early phases of soap system. The important feature of a smectic mesophase, which distinguishes it from a nematic or a cholesteric one, is its stratification. The molecules are arranged in layers and exhibit some correlation in their position in addition to the orientation ordering. The layer can slide easily over one another. Depending on the molecular order in layers, a number of different types of smectic have been observed. Such that the most common are Smectic A and Smectic C.

In a Smectic A, molecules are aligned perpendicular to the layers, without long range crystalline ordering within them. In Smectic C, the preferred molecular axis is not perpendicular to the layers, so that the phases have biaxial symmetry. In Smectic B, there is hexagonal crystalline order within the layers.

A number of compounds have both nematic and smectic mesophases. As a general rule, the lower phases have a greater degree of crystalline order. The nematic mesophase always occurs at a higher temperature than the smectic one; smectic mesophases occur in the following order; A–C–B as the temperature decreases.

SMECTIC LIQUID CRYSTAL AT A GLANCE.

- Molecules are arranged in layers. At any instant of the time the number of molecules within a layer is much more than the number of molecules between the layers.
- Highly viscous as they are closely arranged.
- Fluidity is less.
- Depending on the orientation of the molecules smectic liquid crystals are further classified into different types like smectic A, B, C.

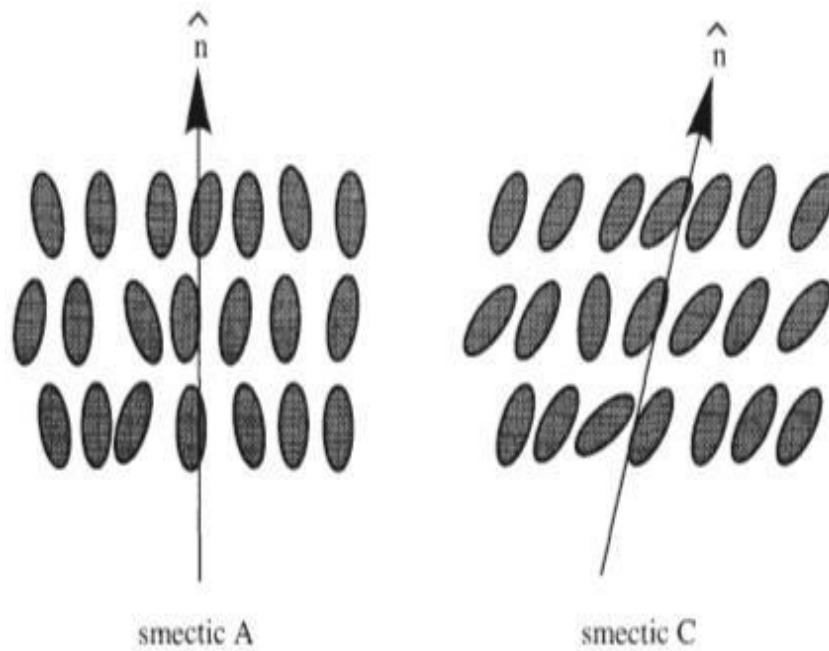


Figure of different type of Smectic liquid crystals are shown above:

CHOLESTERIC LIQUID CRYSTAL :-

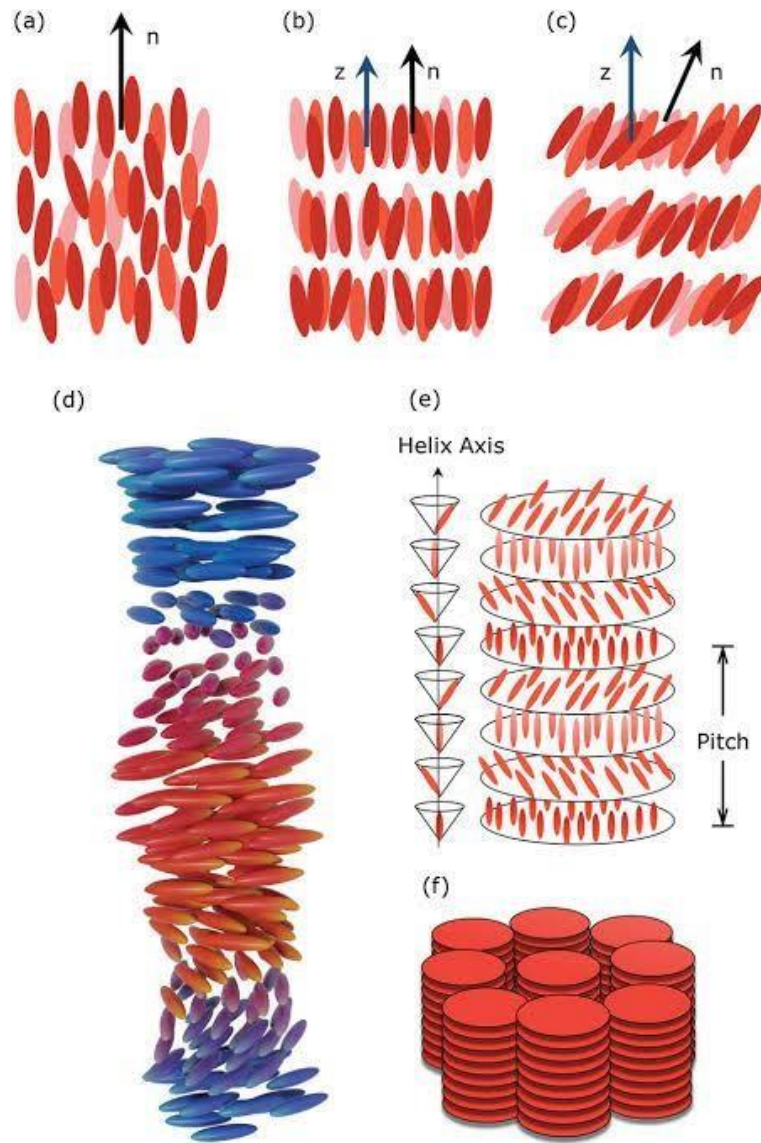
Cholesteric is the nematic state superimposed with a natural twist between layers including the long axis of molecule induced by incorporation of chiral group to give helical twist to the orientation of the Director . The cholesteric mesophase is similar to the nematic it has long range order of the centre of mass of molecule it differs from the nematic mesophase the director varies throughout the medium in regular way even in unstrained state the director distribution is precisely or would be obtained by twisting a nematic aligned along the Y axis about the X axis.

The secondary structure of cholesteric is characterized by the distance measured along the X axis over which the director rotates through a full circle . This distance is called the **pitch** of the cholesteric ,The periodicity length of the Cholesteric is actually only a half of this distance.

Formally a nematic liquid crystal is a cholesteric of an infinite pitch . As a result there is no phase transition between nematic and cholesteric mesophase : nematic doped with enantiomorphic compound become cholesteric of long finite pitch.The molecule forming the cholesteric mesophase have distinct right and left handed forms.

CHOLESTERIC AT A GLANCE:-

- They exhibit finger print texture.
- These are formed from optically active compound.
- A group of molecule is oriented at an angle to the adjacent group of molecule such that the director or take a helical path as it travel through the liquid crystal just as nut is moved to screw.



CHOLESTERIC LIQUID CRYSTALS

A . Dielectric behavior of W-123 :

W-132A(AFLC) is a multicomponent mixture taken from the phase diagram shown in Fig. 1, which has been drawn by mixing two basic multicomponent mixtures, namely, B-2 and K-128. In these two mixtures, the ratio of the different individual components has been tailored to optimize the different physical parameters. Components of B-2 and K-128 with their weight ratio are shown in Table I. Basic mixtures B-2 and K-128 both have a phase sequence of $\text{SmC}^*-\text{SmA}^*-\text{I}$. Figure 1 shows the induction of the SmCA^* phase between 18 and 65 wt % of K-128. It is pertinent to add here that none of the components of B-2 and K-128 possess the SmCA^* phase. The SmCA^* phase has been induced in the present system as a result of intermolecular interactions between terminally fluorinated and hydrogenous compounds. As shown in Fig. 1, the $\text{SmCA}^*-\text{SmC}^*$ transition shows a huge hysteresis of about 5°C which is a common phenomenon associated with the induced SmCA and B-2 in the ratio of 18 and 82 wt %, respectively, as marked by a vertical line in Fig. 1. It is important to mention here that different transition processes of this mixture are quite wide. The phase sequence for W-132A with the transition temperatures in $^\circ\text{C}$ in parentheses is as follows:

Crystal ($<0^\circ\text{C}$) $\text{SmCA}^*-(53^\circ\text{C})\rightarrow\leftarrow(48^\circ\text{C})-\text{SmC}^*\leftarrow(53-59^\circ\text{C})\rightarrow\text{SmA}^*\leftarrow(85-103^\circ\text{C})\rightarrow\text{I}$.

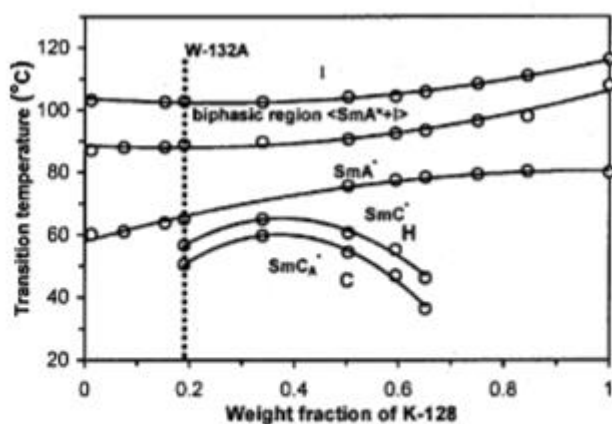


FIG. 1. Phase diagram obtained from two basic mixtures, B-2 and K-128, showing an induced SmCA^* phase. The $\text{SmCA}^*-\text{SmC}^*$ transition (represented by H in the heating cycle and by C in the cooling cycle) shows hysteresis of $\sim 5^\circ\text{C}$.

B. Dielectric Anisotropy of Purified LC Mixtures and Doped with DNPs. :

After purification, all LC mixtures exhibit quite comparable properties, the same optical appearance and equivalent dielectric anisotropy values at 1 kHz . Therefore, the results of doping for only one of these LC mixtures will be presented here in order to avoid redundancy. The dielectric properties of such a representative purified LC mixture doped three different concentrations of DNPs (0.05, 0.1, and 0.2 wt%) were measured. Figure 3 illustrates the real (dielectric constant ϵ') and imaginary (dielectric loss ϵ'') parts of the complex dielectric permittivity, and the dielectric anisotropy. Figure 3 (a)-(c) show two different regions of the real part of the dielectric permittivity for homeotropic and homogeneous alignments. At low frequencies between 0.1 and 10 Hz, when frequency decreases, a significant increase of ϵ' is observed for the purified LC mixture. As explained, this phenomenon is a combination of electrode polarization and electrical conductivity produced from ionic impurities still present in the purified LC sample. On the other hand, doped samples do not reveal a significant increase of ϵ' with decreasing frequency. For samples doped with DNPs, a strong flattening of the slopes of the ϵ' curves is observed compared to the purified LC sample. At frequencies between 10 and 105 Hz, ϵ' remains almost constant for all samples since at such frequencies, the ions as impurities can no longer follow the periodic inversion of the electric field . It should be noted that above 105 Hz, ϵ' decreases for all samples with increasing frequency, for the homeotropic alignment.

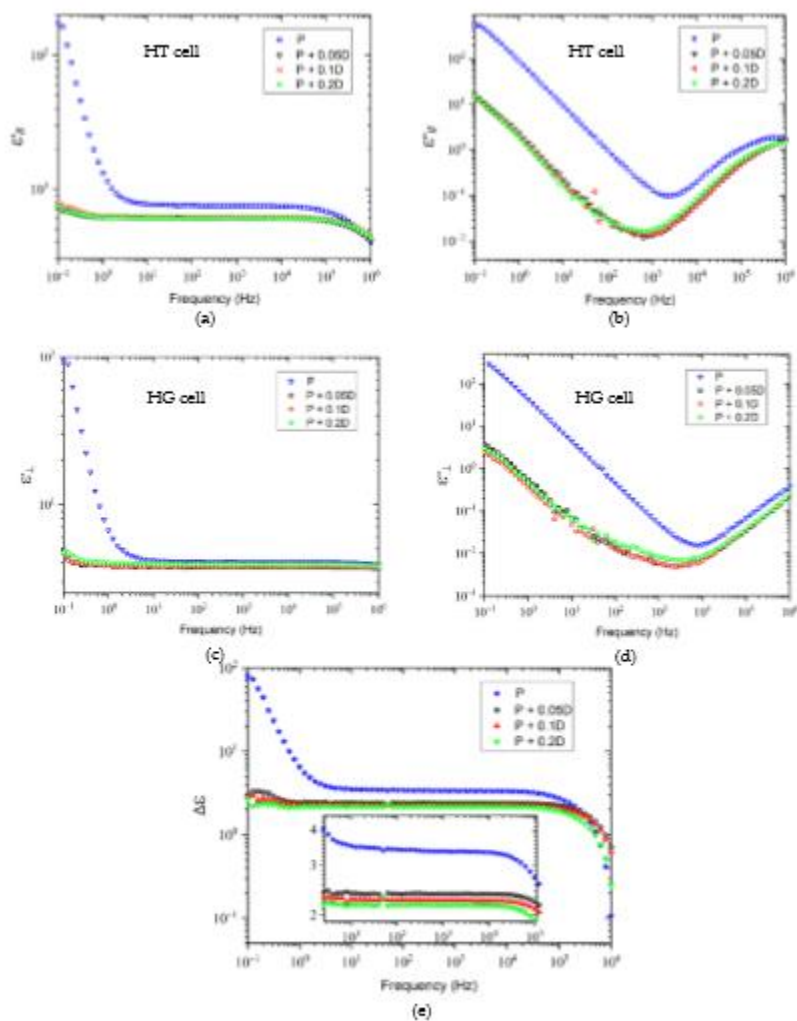


Figure 3. Dielectric permittivity of purified LCs doped with different concentrations of DNPs (0.05, 0.1, and 0.2 wt%): (a) real and (b) imaginary parts in homeotropic alignment, (c) real and (d) imaginary parts in homogeneous alignment, and (e) dielectric anisotropy. The spectra were measured under identical experimental conditions (P stands for purified LC mixtures; P + 0.05D, P + 0.1D, and P + 0.2D correspond to purified LC mixtures doped with 0.05, 0.1, and 0.2 wt% of DNPs, respectively).

C. Dielectric properties of Nicotinic acid/Methyl cellulose composite.

The permittivity ϵ' of cellulose, nicotinic acid and their diffused composite are presented in Fig. 4. The cellulose value is very low if compared to the nicotinic permittivity value. This could be explained based on the chemical structure and nature of nicotinic acid which is composed of carboxyl group attached to pyridine heterocyclic aromatic compound. For our knowledge, the dielectric behaviour only studied in time domain for nicotine compounds in aqueous solutions. However, the dielectric properties here were studied using a frequency domain technique, which was carried out from 0.1 Hz to 1 MHz. The permittivity of nicotinic compound has high value which is 685 at 100 mHz up to 100 Hz, then it decreases gradually until 13.88 at 1 MHz. On contrary, the cellulose compound has the typical average value of methyl cellulose dielectric constant around 8.5 overall the range. However, The permittivity variation of the composite NMC from 140 to 3.5 overall the frequency range 10^{-1} – 10^{+6} Hz reveals that the nicotinic materials have diffused successfully on the cellulose, even is lower than cellulose value itself at high frequencies. This can be explained through the reactivity resistance which is becoming very low at high frequencies rather than cellulose alone. Moreover, the free volume of NMC is decreased and no relaxation or dynamic processes could be produced at high frequency rather than MC alone. The second evidence of the diffusion is the “Maxwell-Wagner-Sillars” MWS effect which appears on low frequency range 100 mHz–10 Hz alongside to the interfacial polarization of methyl cellulose MC. The dielectric loss tangent was measured directly from the broadband dielectric spectroscopy system. In Fig. 5 the dielectric loss tangent against the frequency is shown. The nicotinic compound has two relaxation peaks one for the rotation motion of the whole compound and the second for the carboxylic group rotation motion on short axis as gamma relaxation. The cellulose material has high electrode polarization characteristics due to the presence of the hydroxyl groups. The main peak is covered under the electrode polarization peak as shown in the figure. However, the nicotinic cellulose composite has two peaks as similar as nicotinic acid materials, but both peaks are shifted to low frequency region. This indication is for diffusion H-bonds interaction of the nicotinic acid compound with the cellulose one. The dielectric loss is calculated from knowing the permittivity and the dielectric loss tangent $\tan\delta = \epsilon''/\epsilon'$ for any material as a property of matter. The dielectric loss ϵ'' represents the dissipation factor for the material which elucidates the dissipated part of incident energy and how it was lost inside the material under the test of applying electric field. Therefore, the dielectric loss ϵ'' was plotted against the frequency. The peaks are referring to rotational motions which were taken place using the dissipated energy in specific time as called relaxation time τ_R after removing the applied field. The maximum height of the peaks is called relaxation peak

which is located against the relaxation frequency f_R . In Fig. 6 the relaxation frequency was shifted from high frequency of pure nicotinic acid at 140.6 Hz toward low frequency in the nicotinic acid/cellulose composite to 0.5 Hz. The small relaxation frequency f_R means the long relaxation time τ_R . Therefore, the hindrance of rotational motion increased on the nicotinic acid material due to the composition with cellulose and led to long relaxation time τ_R . However, the loss decreased rapidly to be close to dielectric loss value of cellulose pure sample 0.095 in the high frequencies at 0.5–1 MHz. Additionally, there is a double increase in the loss value at the low frequency (0.1 Hz) from 17.6 for nicotinic to 36.2, but the overall trend of the composite is still lower than nicotinic acid and higher than the cellulose compound. The dielectric loss of cellulose is much lower than other nicotinic compounds, and can be considered a good candidate to the capacitor and storage devices.

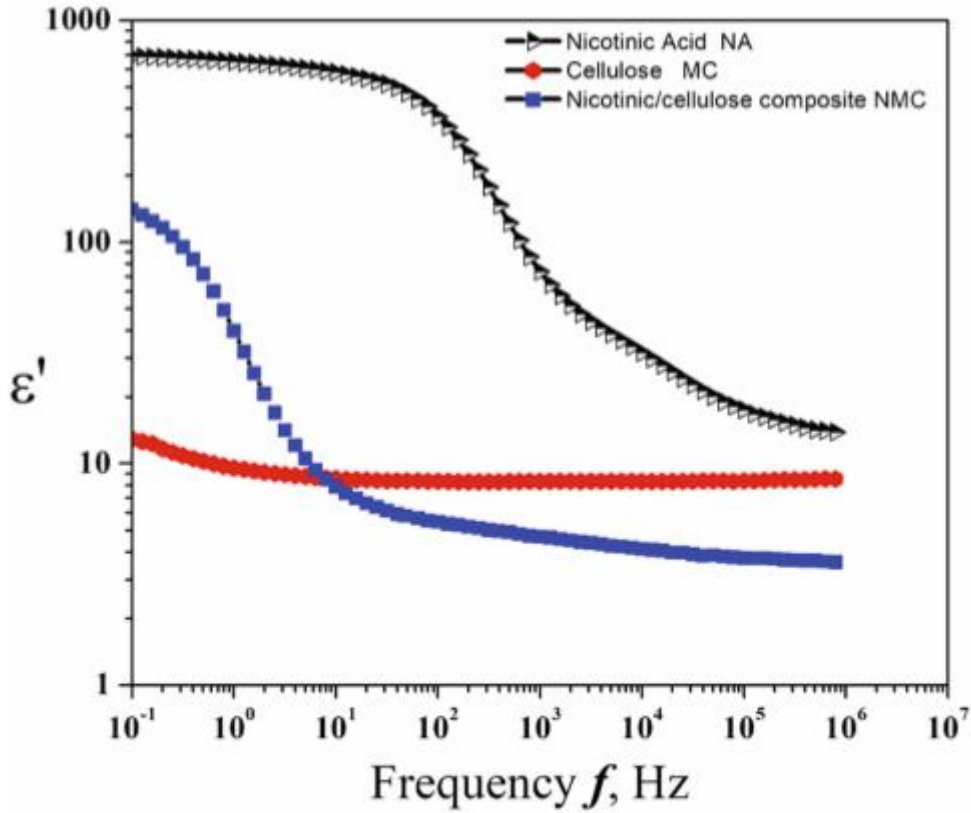


Fig. 4. Dielectric permittivity of cellulose, nicotinic acid and 1:1 ratio of nicotinic/cellulose composite.

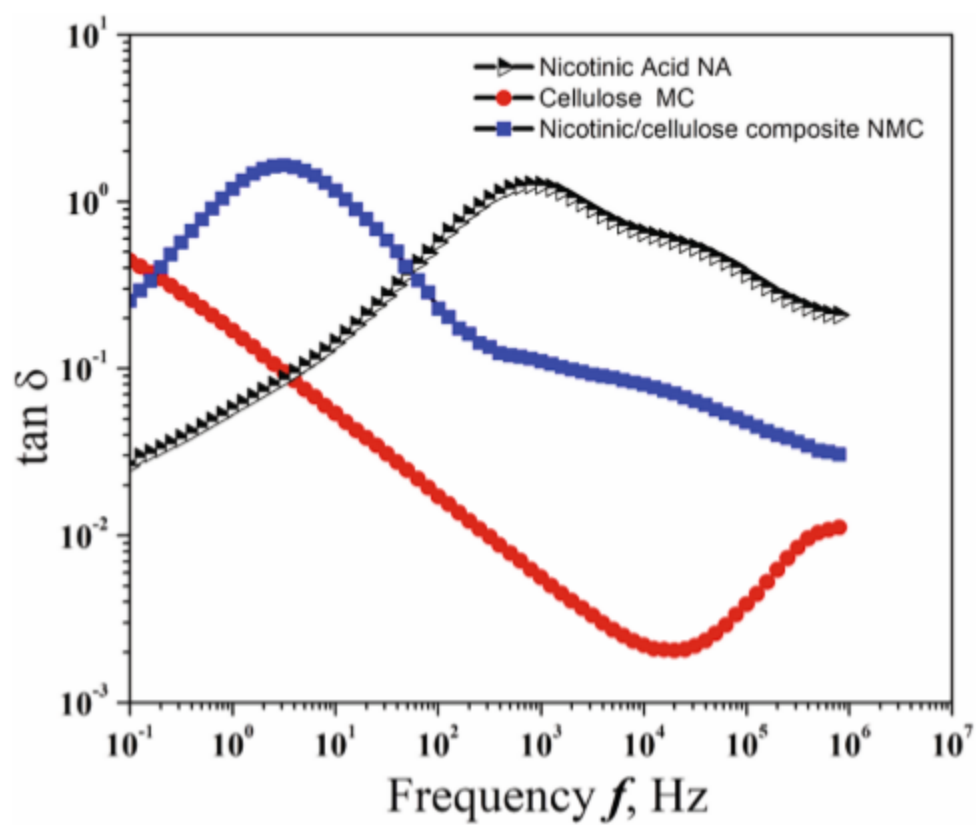


Fig. 5. log-log scale of the tangent loss against the frequency for the cellulose, nicotinic acid and their composite.

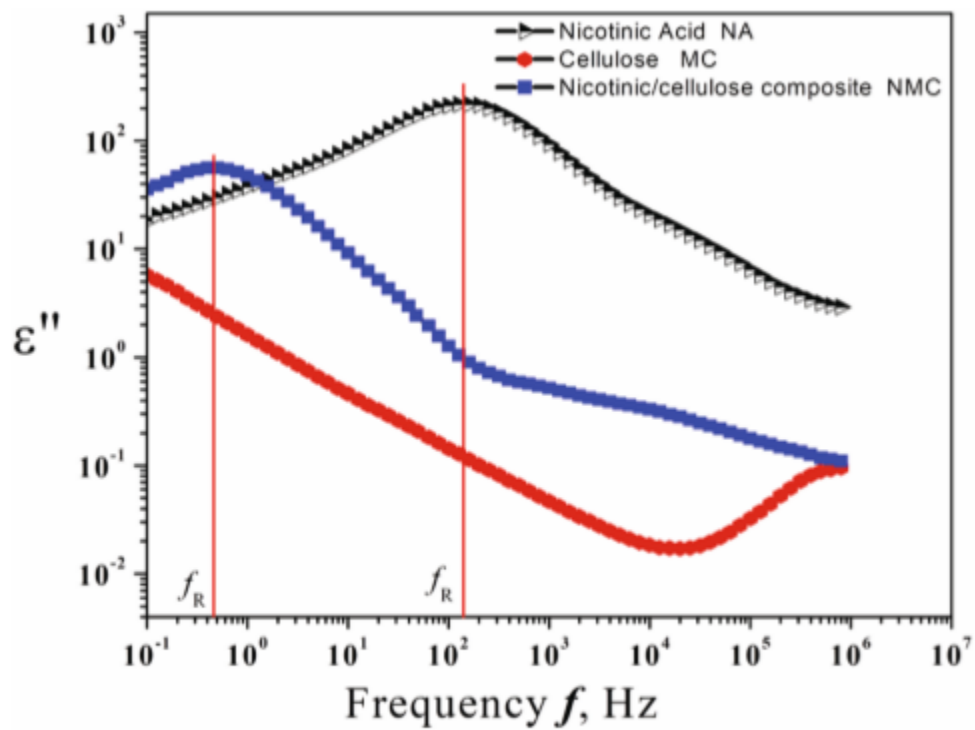


Fig. 6. The log–log scale of the dielectric loss against the frequency for cellulose, nicotinic acid and their composite.

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Citation: Journal of Applied Physics.

2. Dielectric Spectroscopy Analysis of Liquid Crystals Recovered from End-of-Life Liquid Crystal Displays

*Ana Barrera 1, Corinne Binet 1, Frédéric Dubois 2 , Pierre-Alexandre Hébert 3, Philippe Supiot 1 , Corinne Foissac 1 and Ulrich Maschke 1,**

3. Dielectric properties of nicotinic acid/methyl cellulose composite via “green” method for anti-static charge applications

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