

## Study effected Graphene Oxide (GO) on dielectric and conductivity in binary system Liquid Crystals

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### Abstract

Prepared of compound (A) 4,4'-bis-[4-methyl benzyliden]-phenylendiamine-(1,4), and (B) 4,4'-bis-[4-bromo benzyliden]- phenylendiamine-(1,4). Then a binary system D was created with concentration (0-100)% and found less eutectic point at concentration (60%). This was taken concentration from binary system pure D and measurements of a microscopy polarized and permittivity and conductivity. After taking a mixture pure and has been doping by graphene oxide (GO) too the same measurements observed the increase remarkable properties of graphene oxide (GO) in LC mixtures dispersions.

**Keywords:** Liquid Crystals, Graphene Oxide, Dielectric constant, conductivity, nanoparticle.

### الخلاصة

حضر المركبين (A) 4,4'-bis-[4- و (B) 4,4'-bis-[4-methyl benzyliden]-phenylendiamine-(1,4) bromo benzyliden]- phenylendiamine-(1,4) وتم عمل نظام ثنائي من هذين المركبين من (0-100%) ووجد أقل درجة انصهار في التركيز (60%) فتم اخذ هذا التركيز للقياسات ومنها المجهر الضوئي المستقطب و DSC والتوصيلية وثابت العزل الكهربائي عند التردد (400-4000) هرتز علماً بأن جميع القياسات أجريت في الحالة النقية بعد ذلك تم تحضير اوكسيد الكرافين (GO) وتم تشويب النظام الثنائي من البلورات السائلة بهذه المادة النانوية وأجريت لها نفس القياسات السابقة بالحالة النقية وفورنت النتائج فكانت هناك طفرة لافتة للنظر في الزيادة بالتوصيلية وثابت العزل الكهربائي عند تشويب البلورات بالمادة النانوية و مع ارتفاع درجات الحرارة.

### Introduction

#### *Dielectric and conductivity Studies of Graphene Oxide (GO) In Liquid Crystals*

Composites based on liquid crystal (LCs) have attracted much attention over number of years because of their unique electro-and magneto-optic properties and novel display applications[1]. Liquid crystal is the mesomorphic ordered state of anisotropic particles that bears liquid-like fluidity as well as crystal-like ordering[2]. Along with the recent enormous interest in carbon- based liquid crystals hold great promise for high-performance carbon material synthesis or device operation. Liquid -crystalline processing of carbon nanotubes, as well as mesophase pitch, has been employed for highly oriented carbon fibers spinning, graphene oxide liquid crystals are introduced as a versatile new class of carbon-based liquid crystals[3]. Graphene

oxide (GO) have used to fabricate electrodes for the LC device and showed excellent performance with a high contrast ratio. In the present study, we have doped the GO nanomaterial in electric liquid -crystalline electrical (ELC), material. Studying the collective dielectric processes in the GO doped ELC material, the experiments have been carried out on vertical and planar converted samplers using the same samples cell[4].

In spite of high importance of dielectric characteristics for understanding the remarkable properties of graphene oxide (GO) in LC mixtures dispersions, only few studies were focused on this problem[5][6]. Revealed, correspondingly, enhancement of anisotropy of electric conductivity and dielectric constant of LC-GO dispersions due to orientation ordering of GO in LC mixtures[7]. Revealed sharp increase of electric conductivity with GO

concentration, which is caused by formation of continuous network of GO in LC mixtures.

$\epsilon'$  it is frequency dependences of real imaginary, and  $\epsilon''$  it is parts of dielectric permittivity (dielectric spectra) of LC- GO dispersions. According to earlier studies, this approach allows to distinguish different processes of dielectric relaxation improve understanding structural organization and interfacial interaction in the LC-GO systems. Besides, it is important from the methodological point of view, because it gives a correct frequency range to measure electrical conductivity. By analyzing dielectric spectra, we clarify changes in charge transfer mechanisms and electric field distribution within LC cells realized by insertion of GO [8].

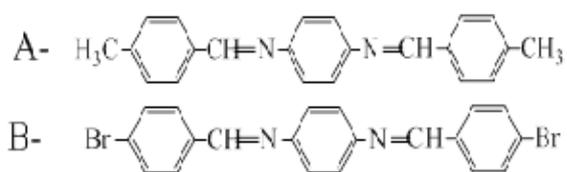
## Experimental Part

### Chemicals material

Graphite, Acetone, Conc. sulphuric acid, Sodium nitrate, Hydrogen peroxide, p-Bromobenzaldehyde, p-Methyl benzaldehyde, Phenlinediamine, Ethanol Absolute.

### Preparation of binary mixtures

The binary mixtures D are composed of (A) 4,4' - bis - [4 - methyl benzyliden] - phenyldiamine - (1,4) and (B) 4,4' - bis - [4 - bromo benzyliden] - phenyldiamine - (1,4). The components have the following structural formula:

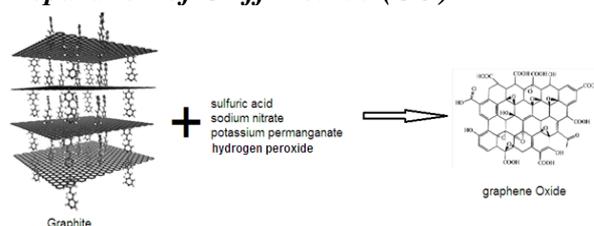


The components (A, B) taken a molar fractions and weighed in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogenous mixture, after which they were cooled. The solid obtained was finally ground and used for determining transition temperatures, by using polarizing microscope fitted with a heating stage[9]. Table 1 shows the melting points and molar fractions with different values of the binary mixtures (D).

**Table 1:** Melting points and a molar fraction of the binary mixtures (D).

Mol % A	M.p (°C)
100	174
90	175
85	173
80	172
75	170
70	169
60	146
50	169
25	185
0	227

### Preparation of Griffin oxide (GO)



**Scheme 1:** Synthesis of Graphene Oxide.

Hummer method was used[10] to oxidize the graphite's for the synthesis of GO as follow: Sodium nitrate (4.0 gm) was dissolved in conc. sulphuric acid (100 ml) at (0 °C) during 15 minutes. To a stirred acidic solution, graphite (4 gm) was added slowly (15 minutes duration). The mixture was kept stirring at (0 °C), and potassium permengante (12gm) was added slowly to the stirred and was cooled mixture (20 minutes duration). The produced mixture was kept stirring at (0 °C) for another 10 minutes. Then it was kept stirring at room temperature for 40 minutes. Distilled water (200 ml) was added very slowly. The solution was heated at (98 °C) for 20 minutes, another amount of distilled water (40-50 °C) was added, and left stirring for 30minutes. Hydrogen peroxide (20-25 %) solution (90 ml) was added to the mixture with stirring (30 minutes), the graphite mixture was filtered several times. The yield was (4.5 gm).



**Figure 1:** Optical photography of a single layer of GO.

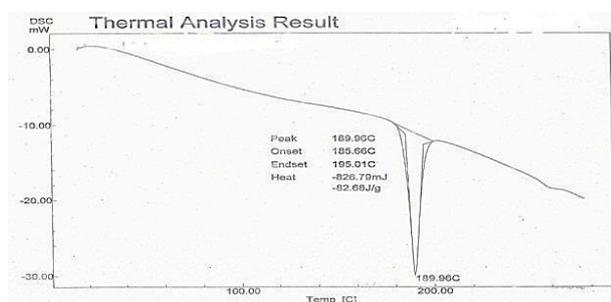
### **Preparation of binary mixtures with Graphene oxide**

Graphene oxide (0.003g) (3) and mixture D {4,4' - bis - [4 - methyl benzyliden] - phenylendiamine - (1,4).[A] + 4,4' - bis - [4 - bromo benzyliden] - phenylendiamine - (1,4). [B]} (0.05g) was dissolved in benzene (10mL). Then mixture was taken to the ultrasound device for 15minutes. Then it was left at room temperature for 24hrs. Then the mixture has transferred to separator. Then leave the solvent to evaporate at room temperature.

## **Results and Discussion**

### **Liquid Crystalline Properties of 4,4' - bis - [4 - methyl - 1,4 - benzyliden] - phenylendiamine [A]**

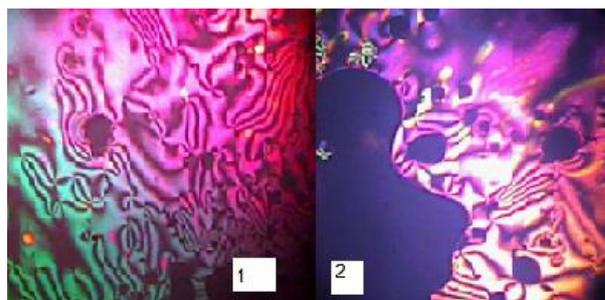
The thermal behavior of 4,4'-bis-[4-methyl-benzyliden]-1,4-phenylendiamine [A] was shown in DSC thermogram Figure 2, and exhibited a peak that represented an actual transition temperature from solid crystal phase to nematic liquid crystalline phase (C → N), at 189.96 °C.



**Figure 2:** DSC thermogram of compound [A].

The optical observation under the hot-stage polarizing microscope of 4,4'-bis-[4-methyl-benzyliden]-1,4-phenylendiamine [A],

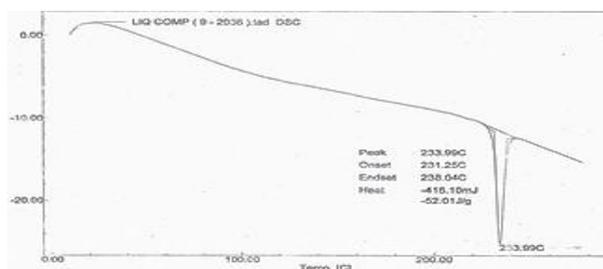
revealed that this compound displayed a nematic mesophase of typical schlieren texture at its liquid crystalline temperature range i.e. above 174 °C, in Figure 3.1 shown texture of a nematic phase planar, at higher magnification. Note that the shape resembles a butterfly, which has the temperature at 218 °C. On further heating these schlieren to form nematic droplets near liquid isotropic transition temperature as shown in Figure 3.2. Liquid isotropic phase has been observed through heating of the compound to 282 °C.



**Figure 3:** 1) Nematicschlieren texture of compound [A] at (218) °C (60X), 2) Transition phase nematic texture at isotropic of compound [A] at (282) °C (60X).

### **Liquid Crystalline Properties of 4,4-bis-[4-bromo-benzyliden]-1,4-phenylendiamine [B]**

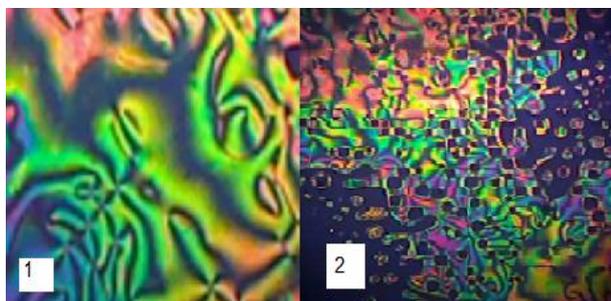
The thermal behavior of 4'-bis-[4-bromo-benzyliden]-1,4-phenylendiamine [B] was shown in DSC thermogram Figure 4, and exhibited a peak that represented an actual transition temperature from solid crystal phase to nematic liquid crystalline phase (C → N), at 233.99 °C.



**Figure 4:** DSC thermogram of compound [B].

The optical observation under the hot-stage polarizing microscope of 4,4'-bis-[4-bromo-benzyliden]-1,4-phenylendiamine [B], revealed that this compound displayed a nematic mesophase of typical thread-like

texture range i.e. above 245 °C as shown in Figure 5.1 On further heating these threads shrunk to form nematic droplets near liquid isotropic transition temperature as shown in Figure 5.2. No liquid isotropic phase has been observed through heating of the compound to a temperature more than 300 °C.

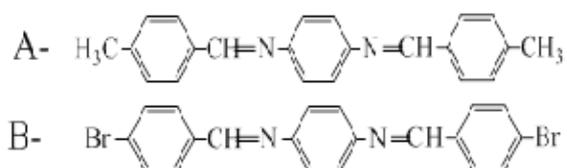


**Figure 5:** 1) Nematic thread-like texture of mode compound [B] at (245 °C) (60X), 2) Transition phase nematic texture at isotropic of compound [B] at (300 °C) (60X).

### Liquid Crystalline Properties and Characterization of mixtures Binary systems

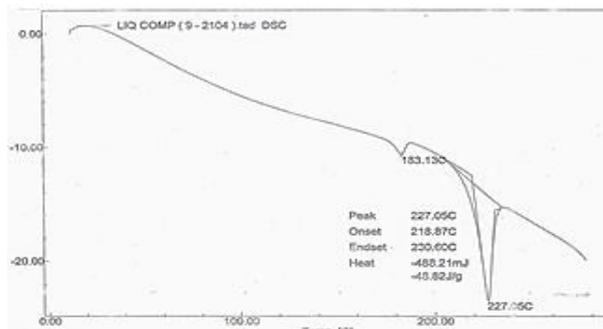
The binary mixtures are composed of two compounds, (A) 4,4' - bis - [4 - methayl benzyliden]- 1,4-phenyldiamine + (B) 4,4' - bis - [4 - bromo benzyliden] - 1,4 - phenyldiamine.

The components have the following structural formula (D):



Liquid crystalline properties of binary mixtures (D) were studied by the DSC thermogram and hot-stage polarized microscope.

The thermal behavior of this compound was shown in DSC thermogram Figure 6 which showed two transition temperatures, the first one at 183 °C belong to the transition from crystal solid to the liquid crystal nematic phase, the second at 227.05 °C liquid crystal nematic phase to the isotropic liquid phase.



**Figure 6:** DSC thermogram of mixtures binary systems (D)

The liquid crystalline property of these mixtures binary systems (D) was studied using hot stage polarizing microscopy where taken molar fractions with different values and as necessitated cases the diagnosis.

**Table 2:** Shows transition temperatures (°C) of mixtures binary system (D) phases.

Mol % A	Cr	→ N	→ I
100	.	174	. 282 .
90	.	175	. 279 .
85	.	173	. 277 .
80	.	172	. 275 .
75	.	170	. 274 .
70	.	169	. 270 .
60	.	146	. 268 .
50	.	169	. 266 .
25	.	185	. 288 .
0	.	227	. 300 .

The Table 2 shows the binary mixture systems between (A) with methyl terminal groups and (B) with strong polar atoms as terminal groups, this show a concave down curve mesophase nematic - isotropic transition temperatures, enantiotropic nematic phase. Figure 7 possessed wide concentration area (0-100 % of A). This system were show the eutectic (E) transition temperature (Cr→N) (146 °C) and (N→I) transition at (268 °C) Figure 7 the concentration region 60 % A (mixture D).

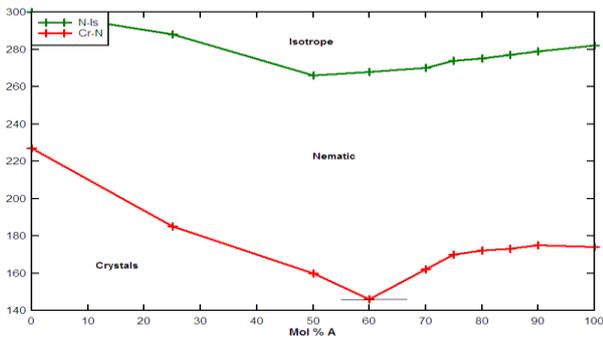


Figure 7: Transitions temperatures of binary system.

### FT-IR Characterization of Graphene oxide

Figure 8 shows several characteristic peaks of FT-IR for Graphene oxide (GO) corresponding to O-H vibration at  $3414\text{ cm}^{-1}$ , C=O stretching at  $1701\text{ cm}^{-1}$ , C=C skeletal vibration from graphitic unoxidized domains at  $1618\text{ cm}^{-1}$ , O-H deformation at  $1325\text{ cm}^{-1}$ , epoxy symmetrical ring deformation at  $1176.58\text{ cm}^{-1}$ , C-O stretching mixed at C-OH bending at  $1070.49\text{ cm}^{-1}$ .

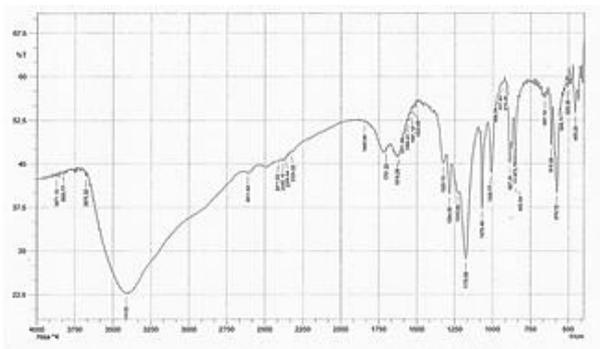


Figure 8: FT-IR Spectrum of Graphene oxide.

### X-Ray Diffraction of Graphene Oxide:

Detailed peak analysis in graphite oxide (GO) Figure 9 shows the spectrum into five peaks with Gaussian–Lorentzian fitting: water like ( $12^\circ \pm 0.3^\circ$ ), GO-related ( $13.1^\circ \pm 0.3^\circ$ ), intermediate ( $25.3^\circ \pm 0.6^\circ$ ), PG ( $27.6^\circ \pm 0.5^\circ$ ) and (100) in-plane ( $43.5^\circ \pm 0.4^\circ$ ) phases. It is noted that the graphite oxide samples show the (100) in-plane phase at  $43.5^\circ$ , indicating a lattice constant of  $1.4\text{ \AA}$  in the plane. Therefore, the graphite oxides retained a lattice constant similar to that of the PG, and thus the graphitic structure of the graphite oxides may not be completely distorted through the oxidation process which was observed in other

experiments[11][15]. The XRD pattern of (GO) Figure 9, show sharp and strong peak at ( $2\theta = 11.70$ ) corresponds to an internal layer distance of ( $7.6\text{ \AA}$ ) (002).

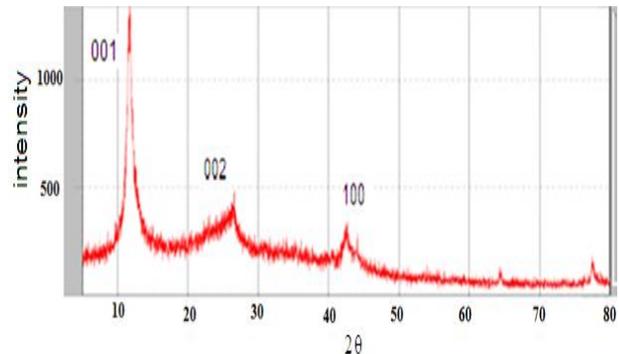


Figure 9: XRD of Graphene Oxide.

### Characterization of nanosheets with Atomic Force Microscope Technique (AFM) and scanning electron microscope (SEM)

It is very important to know the impact morphology and surface of the prepared nanosheets. The Figure 10 show the 2D and 3D AFM image obtained at the surface of the samples. Figure 10 was show the mean value of the maximum height of the nanosheets were lower than  $14.7\text{ nm}$ , the amplitude of the relief was shown lower than  $8.91\text{ nm}$  as inset in Figure 11. On other hand, It is known that the synthesis of graphene materials from reduction of peeling (GO) generally yields samples which are not based on single separated graphene sheets, but rather on an internal connected network in regions of over-lapped multiple layers [16][17].

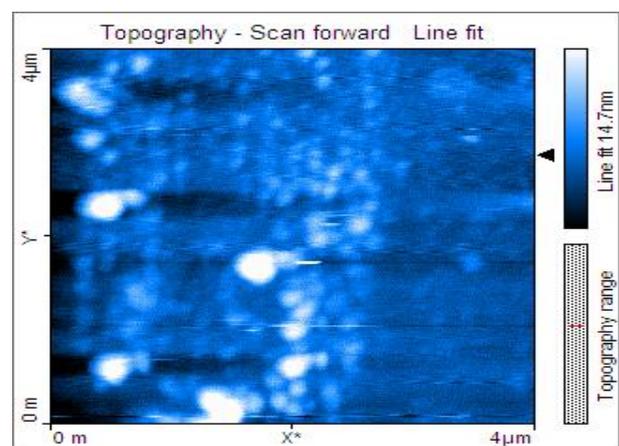
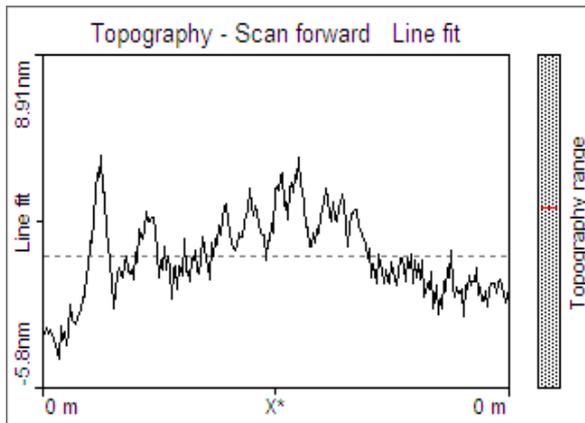


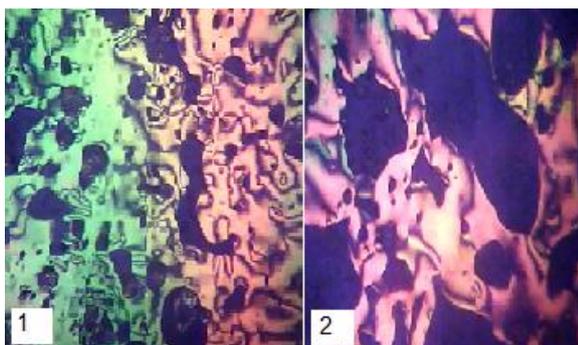
Figure 10: AFM 2D image graphene oxide.



**Figure 11:** AFM topography - scan image of graphene oxide.

### Study the effect of the nanosheets on the liquid crystalline phases

To study the effect of the nanosheets on the liquid crystalline phases, prepared graphene oxide. The addition was at the lower eutectic points of the binary (60 % A) systems. It was worth noting, that in the two mixtures were appeared a new enantiotropic smectic phase. The Figures 12.1, 2 were show the smectic ( $S_x$ ) phase at different temperature. The appearance of the smectic phase may illustrate with reorientation of the liquid crystal molecules. These almost may align parallel to the nanoparticle and functionalized nanoparticles. This particular alignment has two effects: first on is the surface energy and on the interaction between the nanosheets and the liquid crystalline molecules, the latter is smaller than the surface energy. The liquid crystal molecules tend to splay rather than bend around the particle, which decreases the energy since splay was allowed for smectic liquid crystals D[18][20].

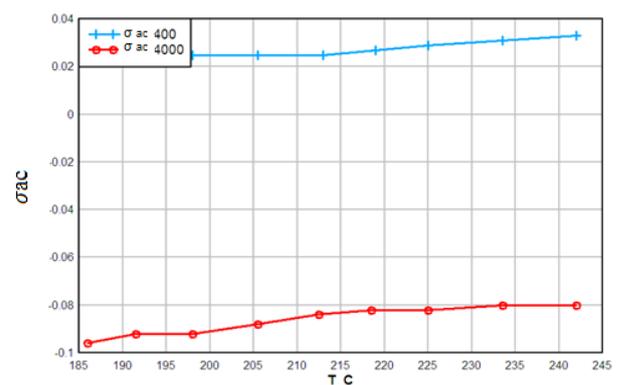


**Figure 12:** 1) Transition smectic at smectic ( $S_x$ ) texture of mix D with graphene oxide functionalized at (220 °C) (60X), 2) Transition smectic at smectic ( $S_x$ ) texture of mix D with garphene oxide at(217 °C) (60X)

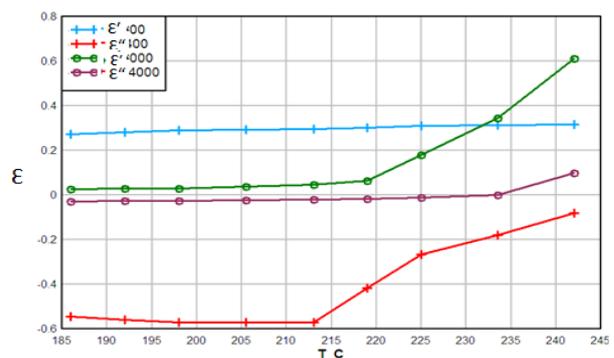
## Electrical Properties of liquid crystals binary systems

### 1. Dielectric permittivity

In this work, the data and figures were divided the data and the figures, each group were showed the results of binary pure system measured in 400 and 4000Hz. The figures were depicted "the real, imaginary-permittivity and the Ac conductivity" of the measurements, these measurements were performed of binary (60 %) pure system measured at the eutectic point concentration with the transition temperatures of Cr-N (146), N-I (268 °C).

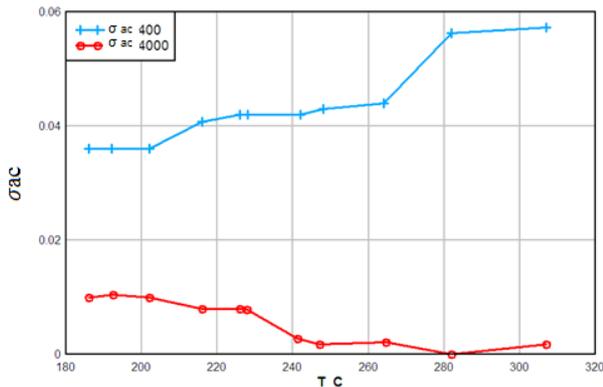


**Figure 13:** Mixture D pure conductivity 400&4000 Hz.

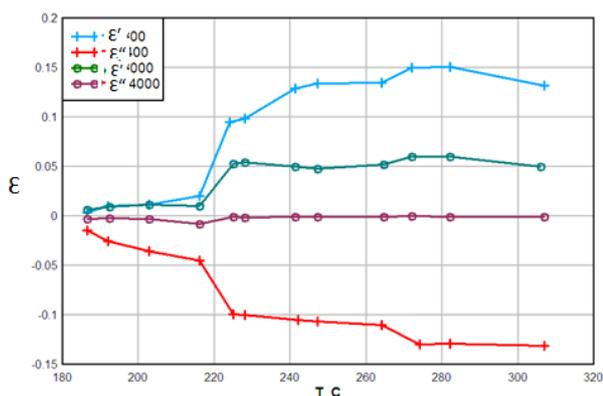


**Figure 14:** Mixtures D pure permittivity 400 4000 Hz.

Figures 13, 14 were show the behavior of pure liquid crystalline mixtures (without nanosheets) of binary and tertiary systems respectively at the eutectic point concentration, the real and imaginary permittivity ( $\epsilon'$  and  $\epsilon''$ ) measured only in the nematic phase. The values of  $\epsilon'$  and  $\epsilon''$  were appeared at 400Hz higher than that value at 4000Hz and  $\epsilon'$  increased with the increasing of the temperature, but  $\epsilon''$  of the binary system with 4000Hz increased with temperature till 225 °C and show a sharp decreasing.



**Figure 15:** Mixture D with graphene oxide conductivity 400&4000 Hz.



**Figure 16:** Mixture D with graphene oxide permittivity 400&4000 Hz.

Figures 15, 16 illustrated the behavior of  $\epsilon'$  and  $\epsilon''$  of binary liquid crystalline mixture systems respectively with graphene oxide nanosheets at the eutectic point concentration (60 %) the measurements were performed in smectic, nematic and isotropic phase. The  $\epsilon'$  was show higher values at the 400Hz than at 4000Hz in both binary systems and increased with increasing of the temperatures. The transitions between the smectic, nematic and isotropic phases measurements were show a clear jumps around the transition points in the values of the  $\epsilon'$  especially at the 4000Hz measurements. The values of  $\epsilon''$  of binary systems were show a higher values at 4000Hz than at 400Hz, in both systems at 400Hz values of  $\epsilon''$  decrease with increasing of the temperatures, and at 4000Hz the binary system show increasing values of  $\epsilon''$ , were rose till 238°C and decreased sharply.

## 2. Conductivity of samples

According to [21][22], dielectric spectra in the middle frequency region B (10-10<sup>5</sup>) Hz characterize bulk properties of the sample.

The resistance R is independent on the frequency in this frequency range in the binary systems for neat LC. The binary system of pure LCs mixtures Figure 13 were not showing any effect at different temperatures on the  $\sigma_{ac}$ , on other hand show the liquid crystals doped with GO nanosheets different results and specially at the transition temperatures in both binary systems Figures 15. The  $\sigma_{ac}$  were show a higher values at 400Hz and were  $S_x < N < I$  phase but in 4000Hz were vice versa for the LC phases  $S_x > N > I$ , and show a jumps at the transition temperatures. This is typical for the free charges transition conductivity of liquid crystals  $\sigma_{ac}$  according to [22].

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