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Electrical Properties of Liquid Crystalline Compounds Doped with Ferric Oxide Nanoparticles Fe_3O_4

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Abstract

Ferric oxide nanoparticles Fe_3O_4 have been prepared and characterized by atomic force microscopy AFM and scanning electron microscopy SEM techniques to determine the particles size and the nature of surface topography. So, the particles size were calculated by Deby-scherrer´s equation. Continuously, liquid crystalline compounds have been doped with that nanoparticles by using different ratios 1%, 1.5%, 2% and 2.5%. then, dielectric permittivity properties, electrical conductivities and activation energies to this doped samples were studied in the range of temperatures at frequency 1000 Hz. Generally, the real dielectric permittivity value increase while imaginary dielectric permittivity values decrease with raising temperature for all percentage ratios of nano doped samples.

Keywords: Liquid crystals, Ferric oxide nanoparticals, Fe_3O_4, Doped, Dielectric permittivity, Electrical conductivities.

1. INTRUDUCTION

The liquid crystalline state is an intermediate state between crystalline regularity and non- regularity isotropic liquid [1,2]. In the liquid crystal phase, the molecules have degree from directional order with different degree of positional order depend on the type of liquid crystal phase [3]. As the component that contain liquid crystal state with different temperature are called thermotropic [4]. It can reorient the direction of liquid crystal compounds by applying an external electric or magnetic field, that attribute to dielectric permittivity and diamagnetic susceptibility[5].

Liquid crystal compounds have very important scientific and large technology applications, but the liquid crystal compound it may be not cover all the scientific requirement from the side of using with devices. For that the study of doping liquid crystals with nanomaterials was interest at the present time, for what these doped are done from advantage in the electrical and magnetic features [6]. It has liquid crystal with inorganic nanomaterials (metals and oxides) common features, electronic features from inorganic compounds magnetism, electrical conductivity and light absorption premium on the liquid crystal represent as fluidity and anisotropy [7].

As the liquid crystals showed in classical devices small value of magnetic sensitivity perhaps these value has increased when it´s doped with materials that are having magnetic sensitivity that is depend on the thickness of the layer which are used in the liquid crystals [5]. Where Rault and his team they has been done the first practical study for the doping liquid crystals MBBA with rod-like ϒ-Fe_2O_3 and the result was obtained ferromagnetic material, premium of low degree of transition temperature from nematic to isotropic phase with increase in the concentration of doped particles [8].

The aim of this research is to prepare Fe_3O_4 nanoparticles for doping liquid crystal compounds and studying the varying of dielectric permittivity, electrical conductivity and activation energy when they are doping with different ratios.

2. MATERIALS AND METHODS

2.1 Preparing of Fe_3O_4Nanoparticles

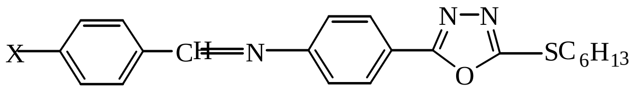
Fe_3O_4 nanoparticles have been prepared by using co-precipitate for Fe^{+2} and Fe^{+3}salts with ratio 2:1 by NH_4OH at temperature (60 °C). The reaction could be followed the chemical equation:

$$2Fe^{+3} + Fe^{+2} + 4OH^{-} \longrightarrow Fe_3O_4 + 4H^{+}$$

(2.8 g) from $FeSO_4.7H_2O$ were dissolved in (100 ml) of distilled water and heated to (60 °C) with vigorous stirring, then preparing another aqueous solution from dissolving $FeCl_3$ in (100ml) of distilled water. The last solution was added to the first then temperature has increased to (80 °C) with using a water bath and after that (20 ml) of NH_4OH have been added to reaction mixture at once time with continuously stirring. After two hours the temperature has been kept at (80 °C) then added a much of distilled water for washing the precipitate that isolated by magnetic decantation, this process repeated more than one time and continuously stirring by magnetic stirrer until getting on equal (pH=7). At last magnetite Fe_3O_4 nanoparticles were dried in vacuum oven.

2.2 Liquid Crystal Compounds

Liquid crystal compounds which studying have been prepared and characterized as previous work [9]. The following scheme show the general structure of the studying compounds.



C = [X-SR_6] (X = Br, Cl, NO_2, CH_3)

2.3 Preparing of Samples

The features of dielectric permittivity have been studied by using LCR meter Model hp-4274A multi frequency, connected with polarized optical microscope (POM) which is having heating platform and using similar glasses cells having areas ($1cm^2$) were painted from one side by Indium Tin Oxide (ITO) which it is electrical conductivity, these cells are work as negative electrode. The studying samples were putted between two the sides of electrical conductivity and filled the samples by the capillary property by heating a little using hot plate and fixed the sample thickness by myler spacer which was (12 micrometer) thickness and then prepared the doped samples by taking weight 1%, 1.5%, 2 % and 2.5% from Fe_3O_4 nanoparticles to liquid crystal compound it has been added the weight percentage in (10 ml) of ethanol, then the solution translated to ultra sonic device to destroy the aggregation that accrued in nanoparticles at last the solvent were evaporated by vacuum oven then doped samples were collected and putted in cells.

3. RESULTS AND DISCUSSION

3.1Characterization of Ferric Oxide Nanoparticles Fe_3O_4

3.1.1 X-Ray Diffraction Technique (XRD)

In the Figure (1) pattern of powder for Fe_3O_4 nanoparticles were recorded by SHIMADZU -XRD-6000, its showing six largest peak of values of 2θ for sure the spinel spherical style for nano Fe_3O_4. As the broadening in peaks refers to small crystallite size. Thus, the nanoparticle size was calculated by Deby Scherrer´s equation [10]. That are supported by full width at half maximum (FWHM) which it is 35.6414 , 62.8334 and 57.2753.

$$L = \frac{0.94\,\lambda}{\beta \cos \theta} \quad \dots\dots\dots\dots (1)$$

Where (λ = 0.167 A°) it’s the wavelength of X-ray which is used, β is the peak width of half maximum in radian and θ is angle diffraction of Bragg´s in degree. Where found the crystallite size of nanoparticles have been found approximately (59.5) nm, (31.8) nm and (39.3) nm.

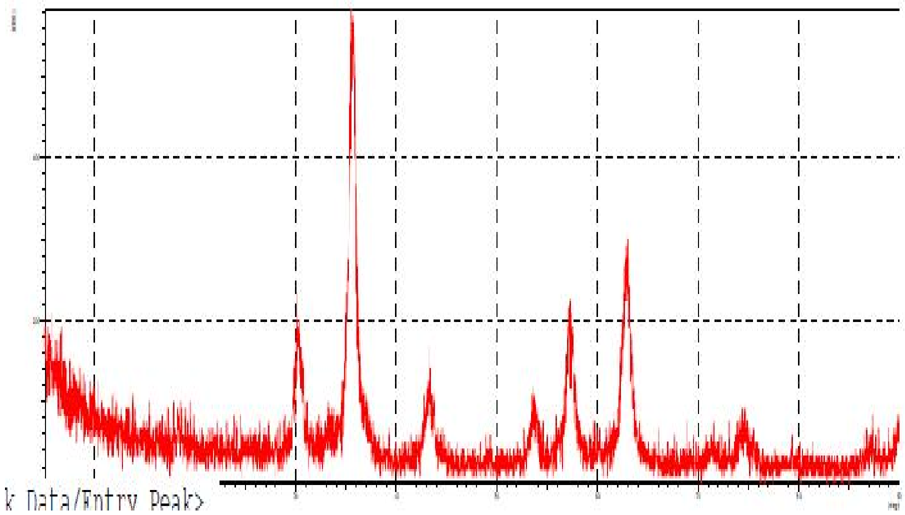


Figure1:XRD pattern of Fe_3O_4 nanoparticles.

3.1.2 Atomic Force Microscope (AFM)

Figure (2) shows both of 2-D and 3-D atomic force micrograph which was obtained by PHYWE compact AFM, that are provided size of nanoparticles approximately (57.2) nm.

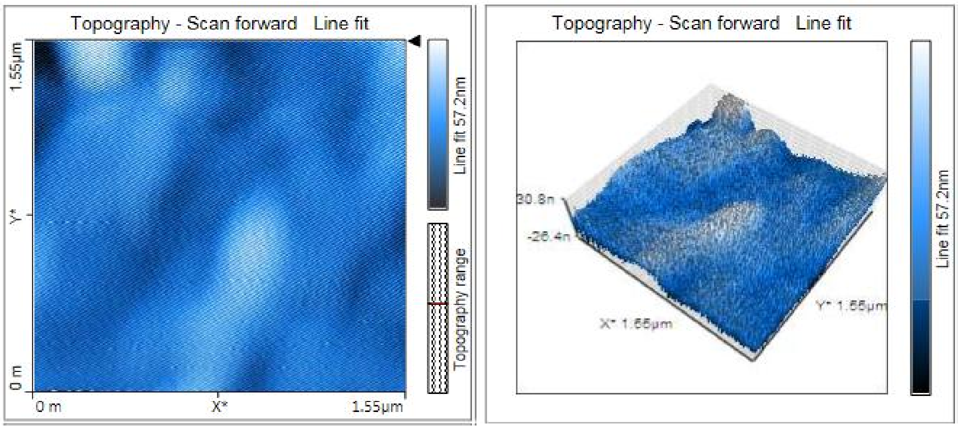


Figure 2: AFM micrographs of Fe_3O_4 nanoparticles.

3.1.3 Scanning Electron Microscope (SEM)

The scanning electron microscope has provided the morphology design and size of Fe_3O_4 nanoparticles as shown in Figure (3) which was obtained by Zeiss instrument, where Fe_3O_4 nanoparticles having spinel spherical shapes are showing big attractions , that is return to high magnetic character for these particles from one side and small size and large area from another side.

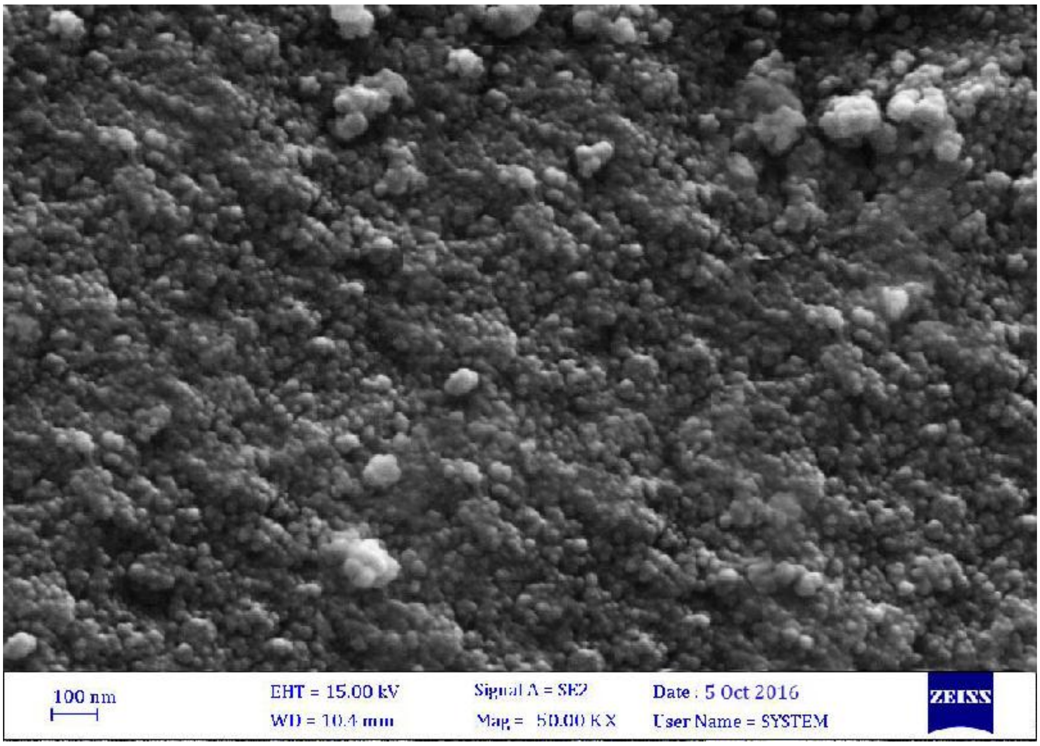


Figure 3: SEM micrographs of Fe_3O_4 nanoparticles.

3.2Electrical Properties

3.2.1 Dielectric Permittivity

The values of real dielectric Permittivity $\acute{\varepsilon}$ have been calculated from measure the capacity of sample C_x proportion to the capacity of air C_a for the liquid crystal samples and their doped with different percentage of Fe_3O_4 nanoparticles at a range of temperature by using the following equations[11,12]:

$$\acute{\varepsilon} = C_x / C_a \quad \ldots\ldots\ldots \ (2)$$

$$C_a = \frac{0.0885\,A}{d} \ldots\ldots\ldots (3)$$

Where A is the area of cell in m^2 its equal (0.001) $m^2$and d is the thickness of samples in cell which equal (12) µm.

Imaginary dielectric permittivity $\ddot{\varepsilon}$ values have been calculated to know the lost amount from real dielectric permittivity in that range of temperatures for doped samples by using following equation [13]:

$$\acute{\acute{\varepsilon}} = tan\delta . \acute{\varepsilon} \ldots\ldots\ldots\ldots (4)$$

where $tan\delta$ is the lost angle which has been founded by using the equation (5) [13,14]:

$$tan\delta = \frac{1}{2.\pi.f.R.C_x} \ldots\ldots\ldots\ldots (5)$$

where π is equal 3.14, f is the applied frequency of electric field, R is the resistance of samples in cell and C_x is the capacity of sample in pF.

Figure (4), (5), (6) and (7) show the values of real dielectric permittivity that increase gradually with increasing temperature, this can be attributed to increasing in thermal motion of liquid crystals doped samples and these values are different from compound to another depending on polarizing of molecules. Thus, the dielectric permittivities are increase as a result to increase of doped percentage with Fe_3O_4 nanoparticles for each compound.

On the other side the value of imaginary dielectric permittivity decrease while the temperature increase for all doped samples that attributed to increase of thermal motion that will cause of decrease the lost value in real dielectric permittivity that are get from oscillating of applied frequency as shows in Figures (8),(9),(10) and (11).

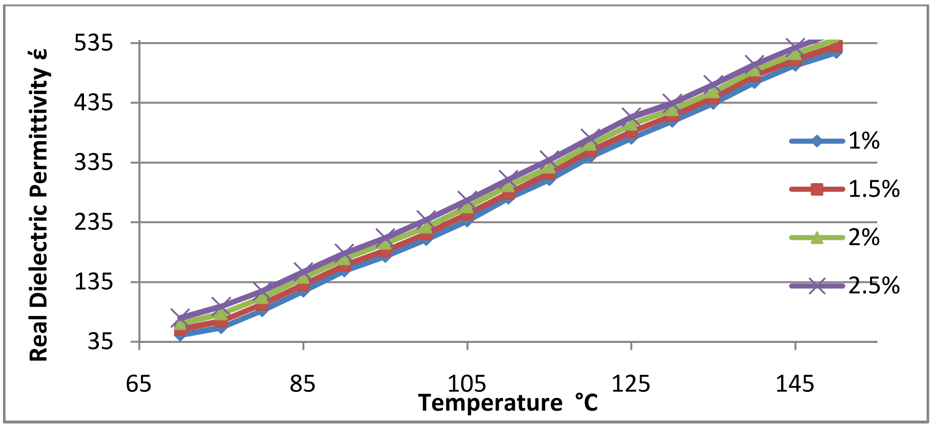


Figure 4: Dependence of real dielectric permittivity of [Cl-SR_6]doped with Fe_3O_4 nanoparticles.

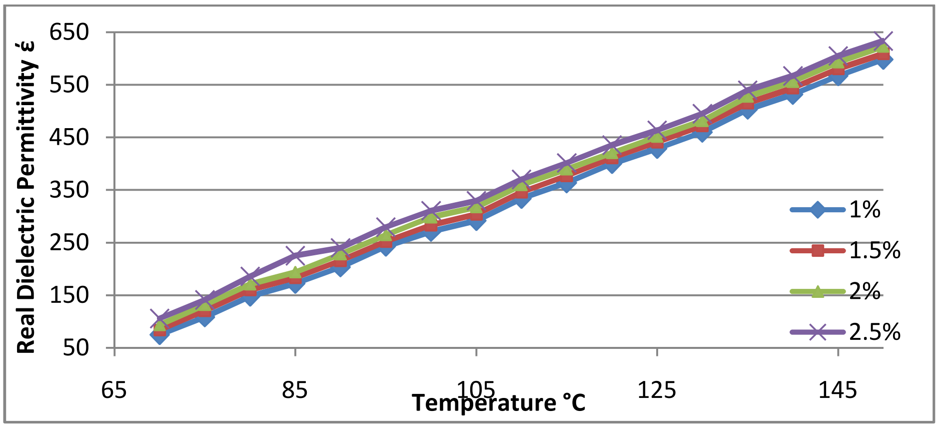


Figure 5: Dependence of real dielectric permittivity of [NO_2-SR_6]doped with Fe_3O_4 nanoparticles.

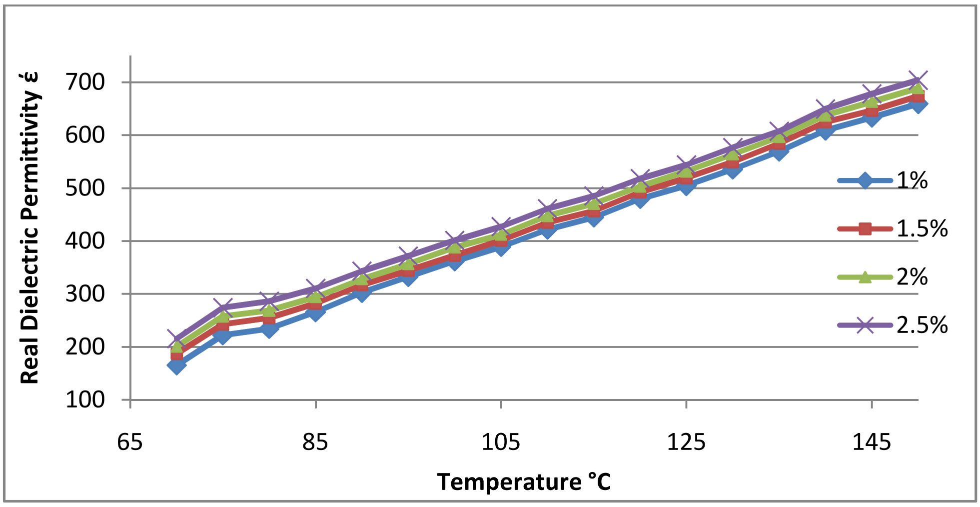


Figure 6: Dependence of real dielectric permittivity of [Br-SR$_6$] doped with Fe_3O_4 nanoparticles.

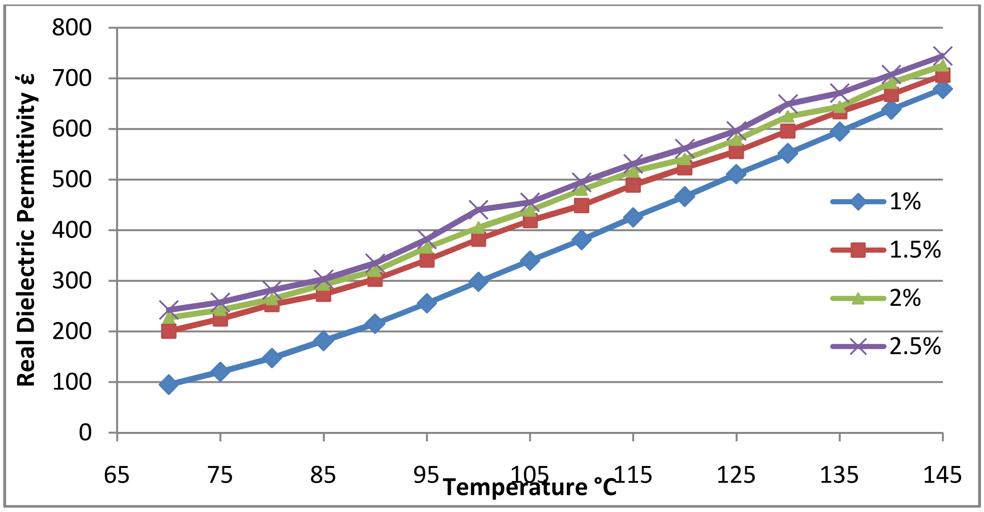


Figure 7: Dependence of real dielectric permittivity of [Me-SR$_6$] doped with Fe_3O_4 nanoparticles.

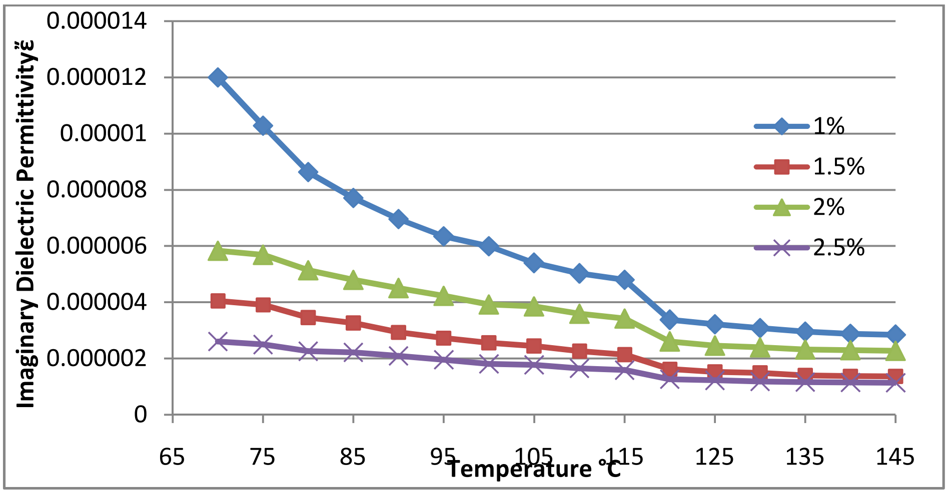


Figure 8: Dependence of imaginary dielectric permittivity of [Cl-SR_6]doped with Fe_3O_4 nanoparticles.

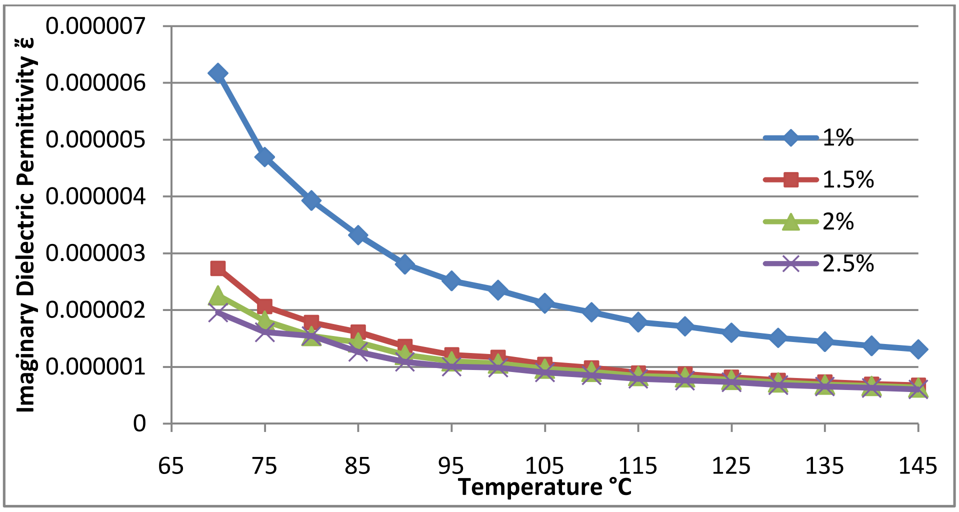


Figure 9: Dependence of imaginary dielectric permittivity of [NO_2-SR_6] doped with Fe_3O_4 nanoparticles.

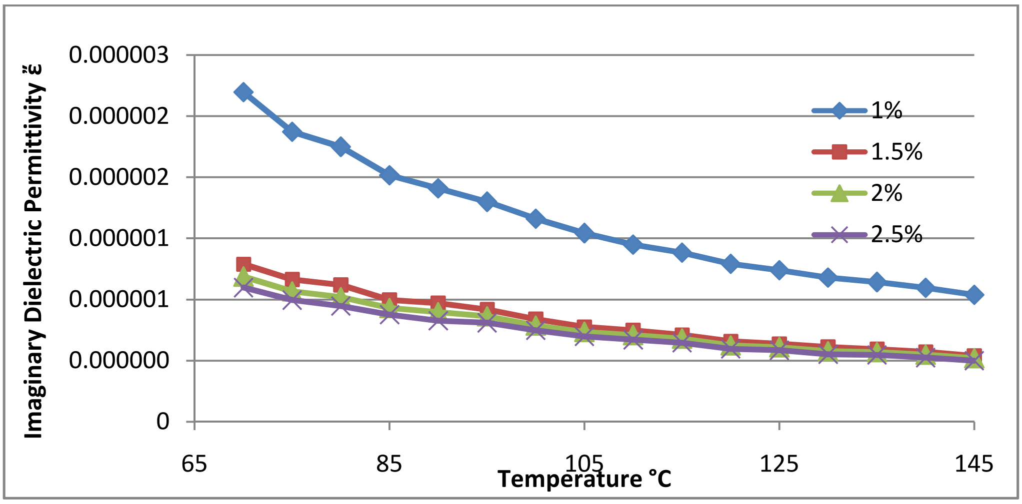


Figure 10: Dependence of imaginary dielectric permittivity of [Br-SR_6] doped with Fe_3O_4 nanoparticles.

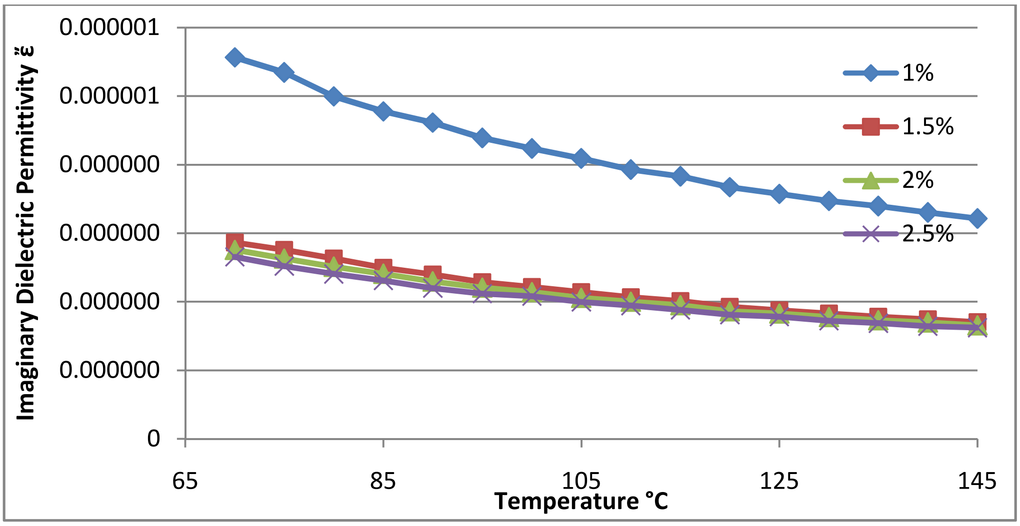


Figure 11: Dependence of imaginary dielectric permittivity of [Me-SR_6] doped with Fe_3O_4 nanoparticles.

3.2.2 Electrical Conductivity

The electrical conductivity σ_{AC} of doped samples has been calculated for the same range of temperature by using the flowing equation [15] :

$$\sigma_{AC} = \varepsilon_0 \, \ddot{\varepsilon} \, . (2.\pi.f) \text{ ……………… } (6)$$

where ε_0 is the free space dielectric permittivity which equal (8.85 * 10^{-12}) F/m.

Figures (12),(13),(14) and (15) show the values of electrical conductivity for doped samples that increase with temperature, so this values are increase with increase of doped percentage with Fe_3O_4 nanoparticles for each compound. Because of the increasing in number of carriers charges which represented in nanoparticles that will simply crossed the gap energy between the equivalent band and conductance band.

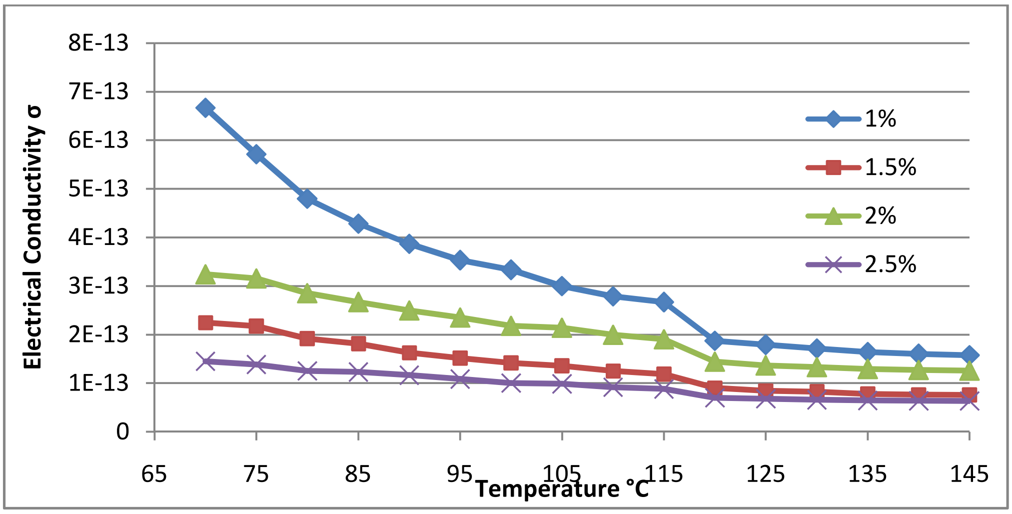


Figure 12: Dependence of electrical conductivity of [Cl-SR_6] doped with Fe_3O_4 nanoparticles.

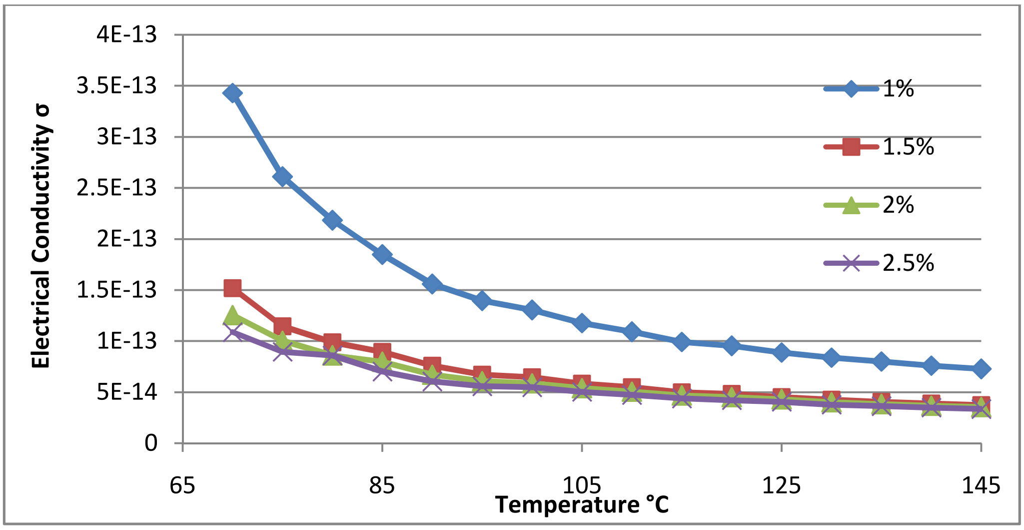


Figure 13: Dependence of electrical conductivity of [NO_2-SR_6] doped with Fe_3O_4 nanoparticles.

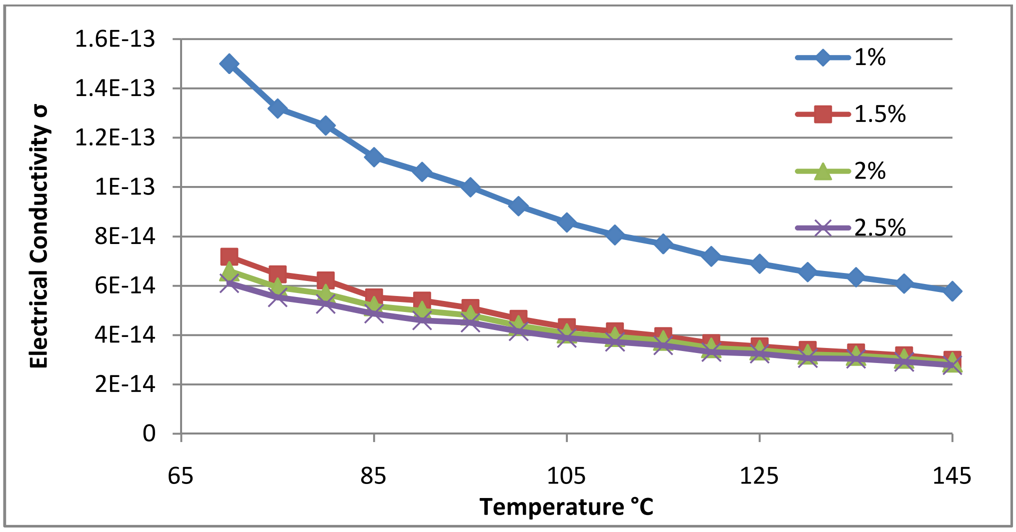


Figure 14: Dependence of electrical conductivity of [Br-SR$_6$] doped with Fe_3O_4 nanoparticles.

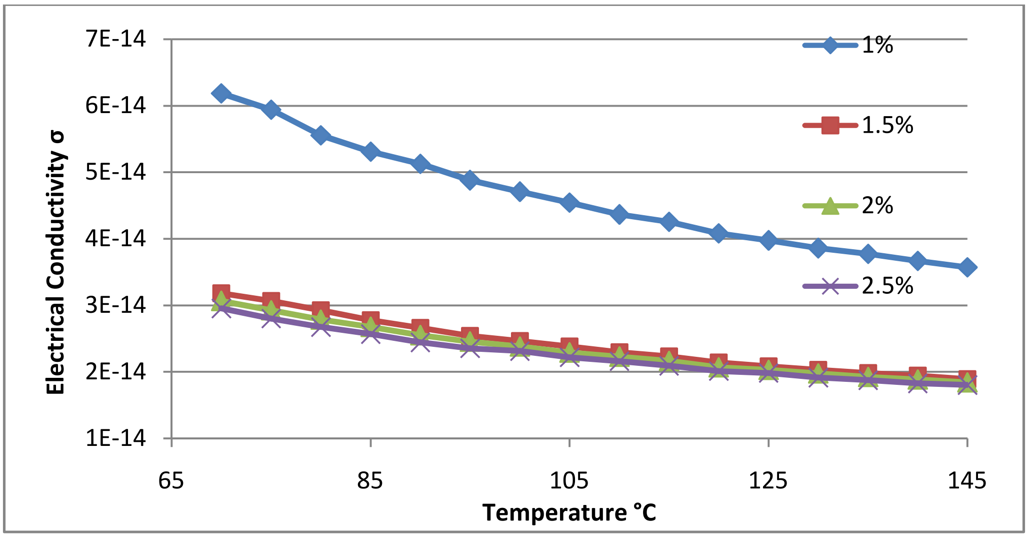


Figure 15: Dependence of electrical conductivity of [Me-SR$_6$] doped with Fe_3O_4 nanoparticles.

3.2.3 Activation Energies

The values of activation energies Ea for doped liquid crystal compounds have been estimated for the same range of temperatures by using Arrhenius´s equation (7) [16] :

$$\sigma_{AC} = \sigma_0 e^{-Ea/k_B T} \quad \dots\dots\dots\dots (7)$$

where σ_0 is the pre-exponential factor, k_B is Boltizmann´s constant and T is the absolute temperature.

This design of Arrhenius´s equation describe the statistical equilibrium to convert clustering of molecules from specific arrangement to another as a result to oscillating of applied frequency which represent the different in potential barrier between the two orientations, while the activation energy represent the amount energy that needed to cross this barrier. Table (1) shows the calculated activation energies.

Table 1: Activation energy values for liquid crystals doped with Fe_3O_4 nanoparticles.

Compound	Ea of 1% doped J/mol	Ea of 1.5% doped J/mol	Ea of 2% doped J/mol	Ea of 2.5% doped J/mol
[Cl-SR_6]	1725.15	1383.45	1216.33	1063
[NO_2-SR_6]	1673.61	1496.52	1366.82	1297.82
[Br-SR_6]	1079.98	996.88	941.14	895.42
[Me-SR_6]	636.68	611.7	590.79	570.83

CONCLUSION

In the present study, magnetite nanoparticles Fe_3O_4 have been successfully prepared by using co-precipitate chemical method. From AFM, SEM and XRD techniques the particles size has been determined was found to be less than (60) nm. Therefore, liquid crystalline compounds were doped with differently ratios of Fe_3O_4 nanoparticles. The electrical properties have been obtained by capacitance measurements. When the ratio of doping increased, the capacitance of liquid crystal materials increased. It can be conclude that doping liquid crystals with magnetite nanoparticles is suitable for technological applications. Because of the magnetic property was increased their response for electrical field through the control of the orientation of liquid crystals.

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