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Electrical Properties on Charge Transfer Complex of Norfloxacin Drug with Iodine Acceptor

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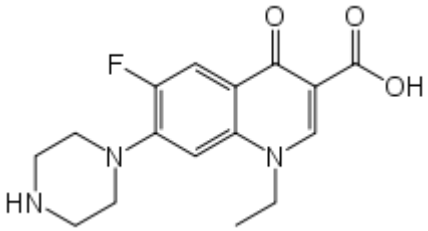
Norfloxacin and iodine were synthesized, structurally and electrically investigated. In the structural investigation, the crystal system and the lattice parameters of the investigated complexes were identified. The electrical properties like AC conductivity and dielectric coefficients were performed as a function of temperature and frequency. Norfloxacin-iodine charge transfer complexes have been recognized to have monoclinic crystal system with different lattice parameters and volumes. Physical parameters such as activation energy, frequency exponent parameter and conduction mechanism of the above antibiotic complexes were estimated. It has been found that the studied complex have resistivity in the order of mega ohm. Meter, by increasing temperature the resistivity tends to decease slightly with a small value of activation energy. On the hand the dielectric constant of this complex was found to be quite high in order of 200.

Keywords: Biomaterials, semiconductors, chemical synthesis, electrical characterization, dielectric properties

1. INTRODUCTION

Norfloxacin (Formula 1) is an antibiotic chemotherapeutic drug [1, 2] which was used in the treatment of urinary tract infections [3].



Formula I: Norfloxacin (nor)

The electron transfer interaction of iodine complexes which were formed between iodine as a sigma acceptor and different kinds of aromatic donors like cyclic amines, hydrocarbons, different crown ethers have been studied and characterized [4–9]. The (I_3) tri-iodide, (I_5) penta-iodide, and (I_9) ennea-iodide ions were prepared upon the chemical reactions of iodine with some of electronic donors like polyazacyclic [10–12] and crown ethers [13–16]. It is worth mentioning that referred to charge transfer reactions have important applications in the field of pharmacological by estimating concentrations of pure and pharmaceutical materials [17]. The charge-transfer in fullerene-based [18, 19] compounds is currently of great interest since these materials can be utilized as superconductors [20] and produce non-linear optical activity [21].

Drugs physical properties are significantly important parameters in such a way that target the infected cells [22]. Polymorphism has become a very significant branch of study either for academic research and pharmaceutical industries [23]. According to the crystal structure the drug has different bioavailability and therapeutic response with cancer and numerous infections caused by bacteria and viruses [24]. In addition, the electrostatic energies stored in the drug play an important role in the attraction or repulsion force against the DNA molecule [25]. Such electrostatic energy is directly correlated to the dielectric constant [26]. Base on the great relationships between the physical properties of drugs and their complexes with industrial applications, this article aimed to prepare a new charge-transfer complex from the chemical interaction between norfloxacin as a fluoroquinolone antibiotics class and iodine as a sigma acceptor. The AC electrical conductivity and the dielectric properties as a function of temperature and frequency were studied.

2. EXPERIMENTAL

Norfloxacin drug was of analytical grade and received from Merck Company. The iodine acceptor was supplied from Sigma-Aldrich Company.

2.1. Synthesis of norfloxacin/iodine complex

The solid CT complex of norfloxacin with iodine(nor/I) was prepared by mixing (0.319 g, 1.0 mmol) of the donor in chloroform (10 mL), A solution of iodine was added (0.254 g, 1.0 mmol) in the same solvent (10 mL) with continuously stirring for about 4 hr at room temperature. An orange yellow

solid was isolated and the solution was allowed to evaporate slowly at room temperature. A solid complex was formed, washed several times with little amounts of chloroform, and dried under vacuum over anhydrous calcium chloride. The empirical formula of this complex is $C_{32}H_{36}F_2N_6O_6I_4$ with molecular weight 1150 g/mol.

2.2. Instrumentation and physical measurements

In this work the CT complex was investigated by using Panalytical X-ray diffractometer which is supplied with CuKα-radiation (λ=1.5418 Å). The operating voltage is 45 KV and the current intensity is 40 mA. The scan speed is 0.005 deg/second, AC conductivity for disk shaped were measured, at room temperature from 0 to 583 K., over wide range of frequency from 50 up to 5MHz, It is to mention that the measurement of dielectric constant was also performed on sample of compressed disk over the same range of temperature and frequency.

3. RESULTS AND DISCUSSION

3.1. X-ray examination

For investigating the crystal structure of the obtained complex, sample in powder form were X-ray examined.

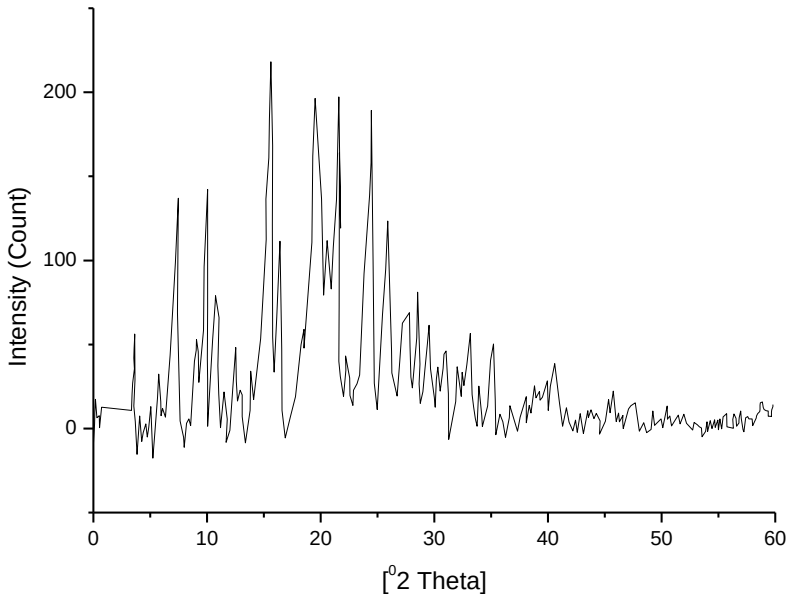


Figure 1. X-ray diffraction pattern of norfloxacin with indexing.

In Fig. (1), the diffraction patter is displayed. Regarding the shown pattern, the samples were in a polycrystalline form. For the lack of the structural data about the investigated materials; CMPR program has been applied in order to index the diffraction pattern. Best fit of the diffraction pattern was carried out to estimate the unit cell and lattice parameters of (nor/I). A Monoclinic unit cell with volume parameters 392.7 $Å^3$, and lattice parameters a=9.90 Å, b= 5.25 Å, and c= 7.75 Å for α= 90°, β= 102.85° and γ= 90° respectively was recognized.

Table 1. Lattice parameters, unit cell volume and X-ray data of $[(nor)_2I^+].I_3$ complex.

	system	a Å	b Å	c Å	h	k	l	V ($Å^3$)	2Θ	d-obs	d-calc
Norfloxacine-Iodine complex	monoclinic	9.9	5.25	7.75	1	0	0	392.5	4.22	9.651	9.6549
					0	0	1		5.38	7.5588	7.5592
					1	1	1		10.84	3.7598	3.7528
					$\bar{1}$	1	2		13.21	3.0873	3.0660
					$\bar{3}$	0	3		18.25	2.2408	2.221
					$\bar{4}$	2	2		23.85	1.7198	1.653
					$\bar{2}$	2	4		26.61	1.5437	1.5325
					2	3	2		28.03	1.4674	1.456

In table (1), the corresponding lattice parameters, volume and X-ray data of the $[(nor)_2I]^+.I_3^-$ system are given. The lattice constants a, b, c, α, β and γ were confirmed with the corresponding hkl using the following equation [27], where the volume V is equal a*b*c*sinβ [28]

For monoclinic system

$$d_{hkl} = \frac{\sin\beta}{\sqrt{\frac{h^2}{a^2} + \frac{l^2}{b^2} + \frac{k^2\sin^2\beta}{c^2} - \frac{2hl\cos\beta}{ac}}} \quad \text{.....(1)}$$

3.2. Electrical and Dielectric properties

Both the AC conductivity σ and dielectric constant of samples of the norfloxacin complexes in form of disk were measured at room and elevated temperatures up to 150 °C.

3.2.1. AC conductivity

The AC conductivity as a function of temperature is shown in Fig. (2) at constant field frequency equal 1MHz .It can be noticed that the conductivity tend to increase slightly with increasing temperature. It can also be seen that the (nor/I) complex has very small conductivity value in order of $5.5x10^{-5}$ $(\Omega m)^{-1}$. The increase of conductivity of $[(nor)_2I^+].I_3^-$ complex with temperature indicates that

the complex behaves as a semiconductor. It can also be noticed that there are two regions in the variation of conductivity against temperature. Region 1 is located in the temperature range between room temperature up to 322 K. Region 2 has a temperature range above 322 K. Such regions can be referred to many mechanisms that might occur. These mechanisms are the decomposition of the complex, the transition from the intrinsic semiconductor to an extrinsic semiconductor and phase change. From the slope of the different parts of the line shown in Fig. (2), the activation energy was calculated at different temperature ranges.

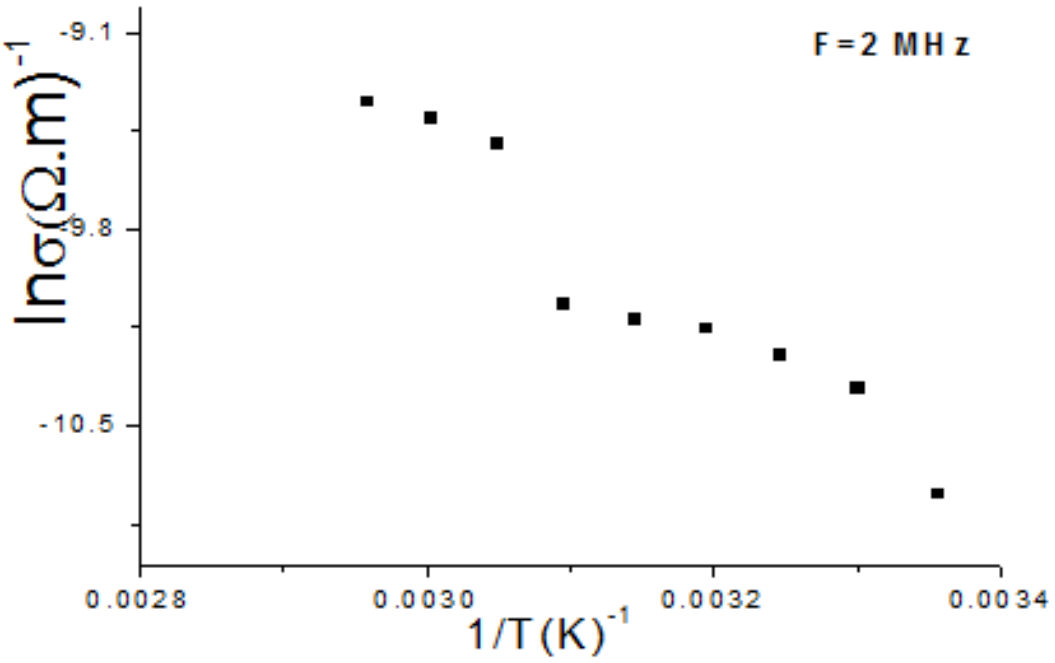
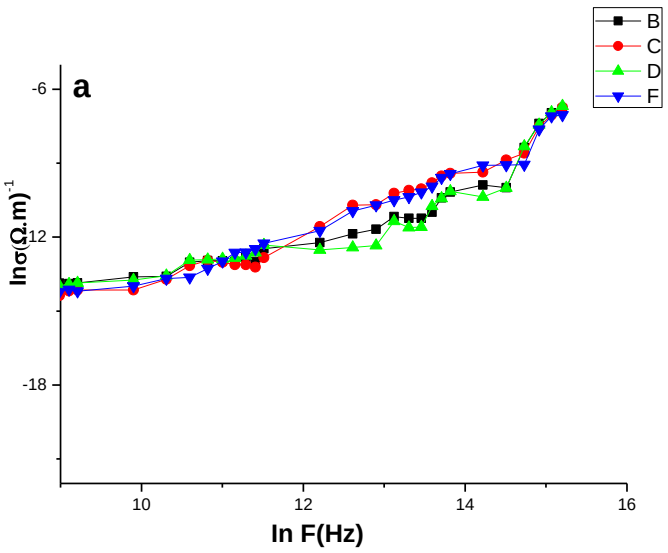
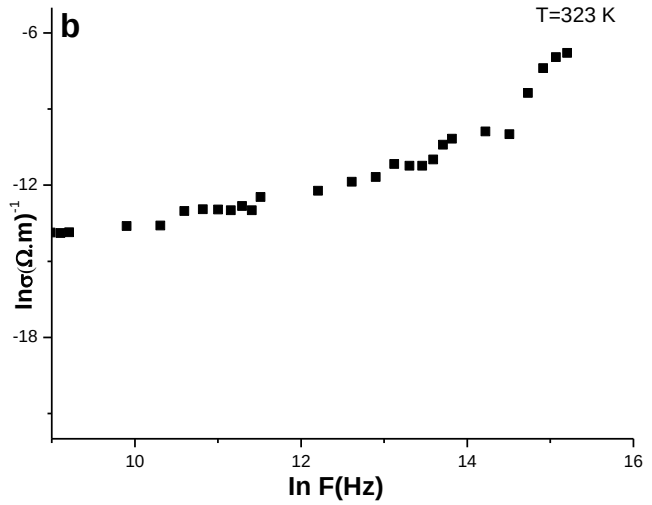
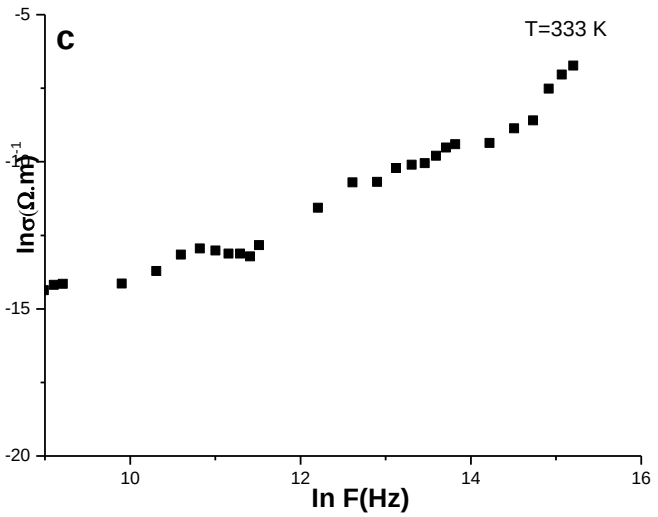
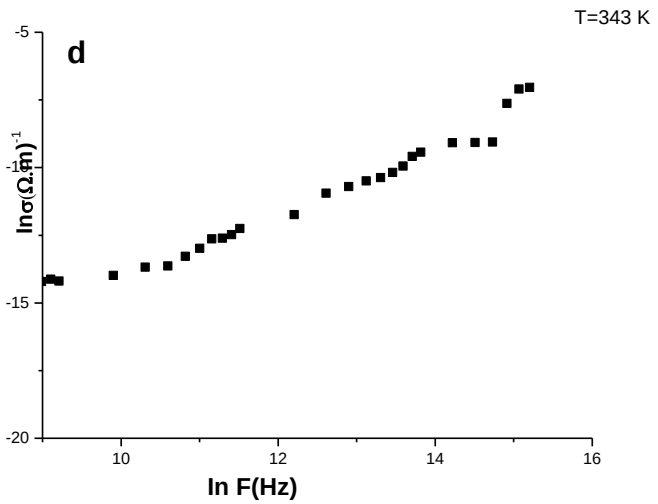


Figure 2. AC conductivity at different temperature T(K) and frequency at 1 MHz for $[(Nor)_2I^+].I_3^-$ complex.




b
T=323 K
-6
-12
-18
lnσ(Ω.m)-1
10
12
14
16
ln F(Hz)


c
T=333 K
-5
-15
-20
lnσ(Ω.m)-1
10
12
14
16
ln F(Hz)


d
T=343 K
-5
-15
-20
lnσ(Ω.m)-1
10
12
14
16
ln F(Hz)

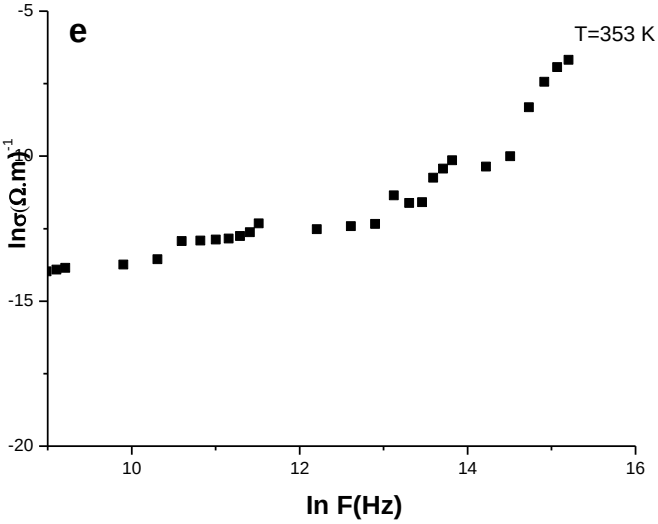


Figure 3(a-e). Frequency dependence of AC conductivity at different temperature for $[(nor)_2I^+].I_3^-$ complex.

In temperature range from 60 – 80 ^oC, the activation energy ΔE was calculated according to the expression :-

$$\sigma_{(T)} = \sigma_0 e^{-\Delta E / K_B T} \quad \text{.....(2)}$$

where $\sigma_{(T)}$ is the conductivity at temperature T and σ_0 is pre-exponential factor.

In the above equation K_B represents Boltzmann constant and T is the temperature in K. From the calculations it has been found that ΔE equal 0.1 eV. Similar calculations were done at different values of frequency of the external electric field and ΔE was found to take random values between 0.1 and 0.3 eV., the average value of the norfloxacin is about 0.2 eV. Similar measurements were carried out at different frequencies of the applied external electric field at constant value of temperature. Fig. (3 a-e) is an example represents the frequency dependence of AC conductivity of $[(nor)_2I^+]$ .I_3^- complex at different temperature. One can observe that the AC conductivity tends to increase with the increase of frequency. In other words the $[(nor)_2I^+].I_3^-$ complex conductivity shows dispersion at the studied range of temperatures. According to this dispersion the conductivity versus frequency verifies the following expression [29].

$$\sigma_T(\omega) = \sigma_{dc} + B\,\omega^{S} \quad \text{.....(3)}$$

where $\sigma(\omega)$ is the AC conductivity, ω is the angular frequency which equals $\omega = 2\pi f$, s is called frequency exponential factor and B is constant. The frequency exponential factor, s can be obtained by plotting $ln\ \sigma_{(\omega)}$ against ln ω along the dispersion region where a straight line is produced. From the slope of the obtained straight line, s has been obtained for $[(nor)_2I^+].I_3^-$ and found to vary between 0.4 up to 0.79. Such value of s is in agreement with the reported values for s which takes values between 0.1 to 1.0. It has been recognized that the mechanism of conduction can be concluded from the trend variation of s against temperature.

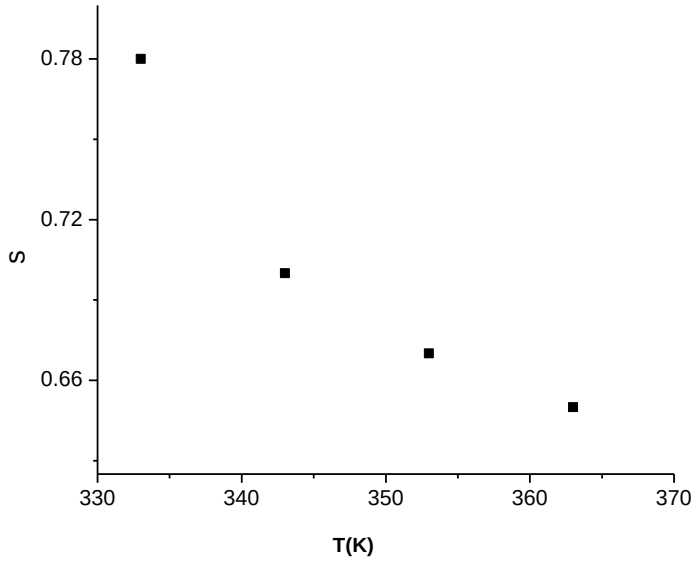


Figure 4. Variation of the exponent factor s against temperature for $[(nor)_2I^+].I_3^-$ complex.

For $[(nor)_2I^+].I_3^-$ complex, s was found to decrease with the increase of temperature as shown in Fig. (4). According by the conduction mechanism is suggested to be correlated barrier hopping (CBH). According to this model s can be written as [30]

$$s = 1 - (6K_B T / w_H) \quad \text{.....(4)}$$

where w_H is called barrier height substitution for K_B, T and s, w_H was calculated for $[(Nor)_2I^+].I_3^-$ complex and found to be 0.55 eV at T= 323 K.

3.2.2. Dielectric properties

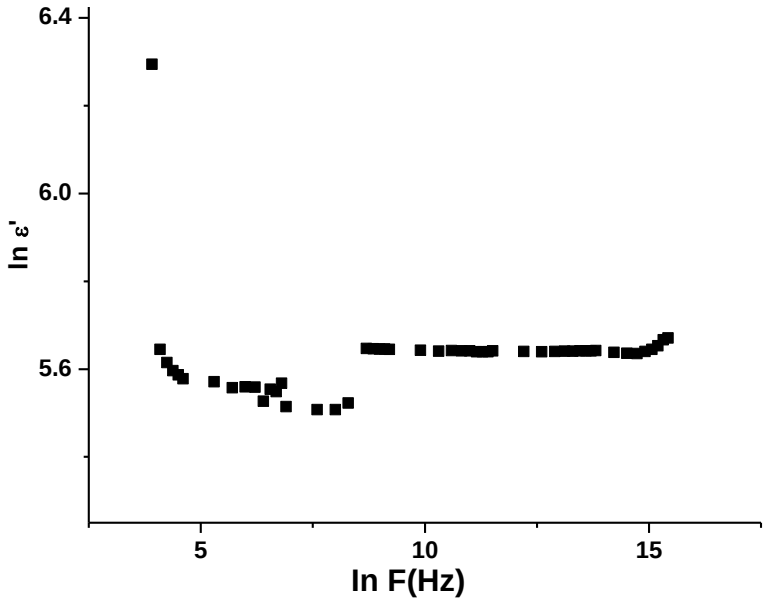


Figure 5. Frequency dependence of dielectric constant at 323 K for $[(nor)_2I^+].I_3^-$ complex

In this study the dielectric constant and the dielectric loss were measured against frequency and at different temperatures. Fig. (5), represents the frequency dependence of the dielectric constant for $[(nor)_2I^+].I_3^-$ complex at different temperatures. It is clear that the dielectric constant of $[(nor)_2I^+].I_3^-$ complex is relatively of high value about 270. As shown in Fig. (5), the dielectric constant seems likely to be frequency independent at high frequency. At low frequency the dielectric constant tends to decrease sharply from about 630 to 330 at 323 K. Such a trend of the variation of έ with frequency may be attributed to the polarization resulting from the heterogeneous structure, the donor and acceptor. On the other hand, The independence with the applied frequency above 150 Hz may be ascribed to low mobility of charge carriers which can not follow the applied field. Figure (6 a-b), represents the frequency dependence of the dielectric loss at two different temperatures 323 K and 353 K. It can be noticed that the dielectric loss of $[(nor)_2I^+].I_3^-$ complex is continuously decreasing with increase frequency in the range of studied frequency.

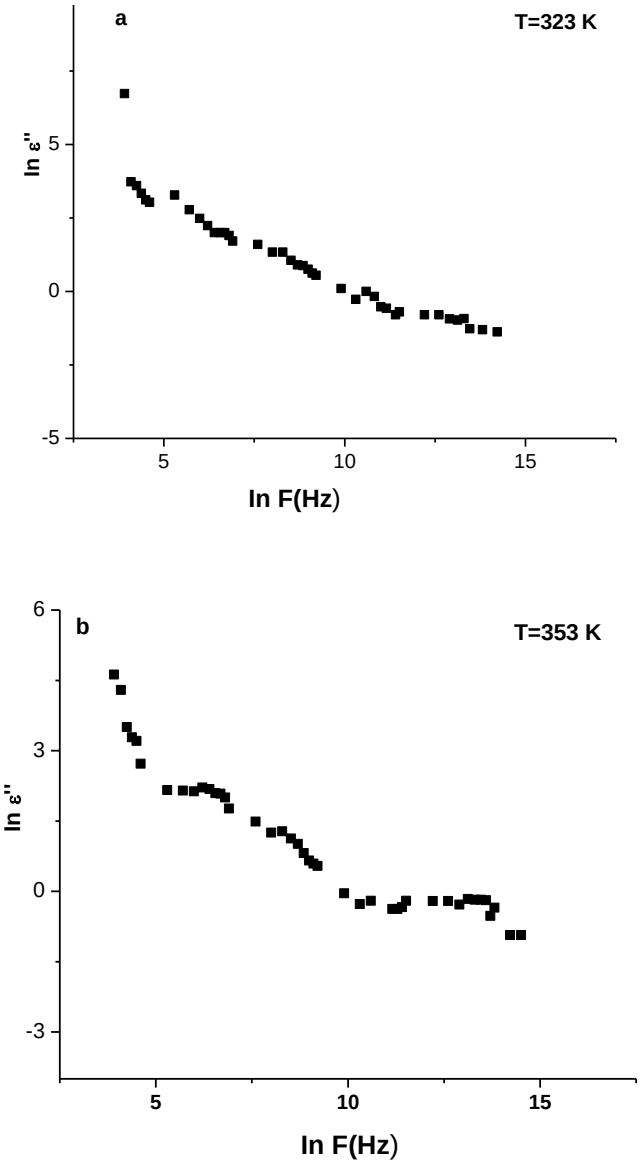


Figure 6 (a,b). Frequency dependence of dielectric loss at different temperature for $[(nor)_2I^+].I_3^-$ complex.

4. CONCLUSIONS

Following are the conclusions that can be revealed:

1-$[(nor)_2I^+].I_3^-$ complex have lattice parameters as a=9.90 Å, b= 5.24 Å and c= 7.75 Å., for $\alpha= 90^o$, $\beta= 102.85^o$ and $\gamma= 90^o$

2- $[(nor)_2I^+].I_3^-$ complex behaves as semiconductor material.

3- Regarding the activation energy for the studied complex $[(nor)_2I^+].I_3^-$.

4- In addition, the conduction mechanism for the studied complex is considered to be due to correlation barrier hopping.

5- The dielectric constant of $[(nor)_2I^+].I_3$ is of relatively high, about 250 .

6- At low frequency, The dielectric constant of $[(nor)_2I^+].I_3^-$ tend to decrease sharply, may be due to the polarization resulting from the heterogeneous structure.

7- The dielectric constant of $[(nor)_2I^+].I_3^-$ seems to be frequency independent at high frequency, may be ascribed to low mobility of charge carriers which can not follow the applied field.

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