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Electrical and Dielectric Properties of Charge Transfer Complexes: Interactions between Norfloxacin and Ciprofloxacin with Picric Acid and 3,5-Dinitrobenzoic Acid[1]

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Abstract—Semiconductor behavior was observed for all three studied complexes. The dielectric constant for [(Nor)(PA)], [(Cip)(PA)], and [(Nor)(DNB)] seems to be frequency independent at high frequency, that may be attributed to low mobility of charge carriers which can not follow the applied field.

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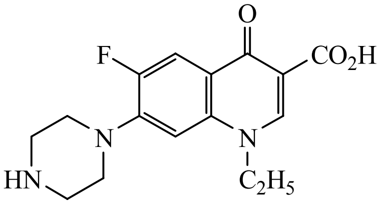
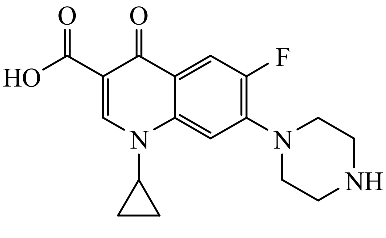
INTRODUCTION

Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [1, 2]. These complexes draw great attention as non-linear optical materials and electrical conductivities [3–6]. Drugs physical properties are also significantly important parameters in such a way that target the infected cells. Polymorphism has become a very significant branch of study either for academic research and pharmaceutical industries. Depending on the crystal structure a drug has different bioavailability and therapeutic effect on bacteria. In addition, the electrostatic energies stored in a molecule play an important role in the attraction or repulsion force against the DNA molecule. Such electrostatic energy is directly correlated with the dielectric constant.

In this paper, we describe synthesis and studying of electrical and dielectric properties of change transfer complexes formed by two fluoroquinolone-class antibiotics, Norfloxacin (Nor) and Ciprofloxacin (Cip) [7–9].



Norfloxacin (Nor)



Ciprofloxacin (Cip)

EXPERIMENTAL

All chemicals used throughout this work were Analar or extra pure grade. Ciprofloxacin (Cip), was of analytical reagent grade (Merck reagent). Stock solutions of Ciprofloxacin or of picric acid were freshly prepared and the spectroscopic grade methanol was used as received.

Norfloxacin-(PA and DNB) complexes. Solid CT complexes of Norfloxacin with picric acid (2,4,6-

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[1] The text was submitted by the authors in English.

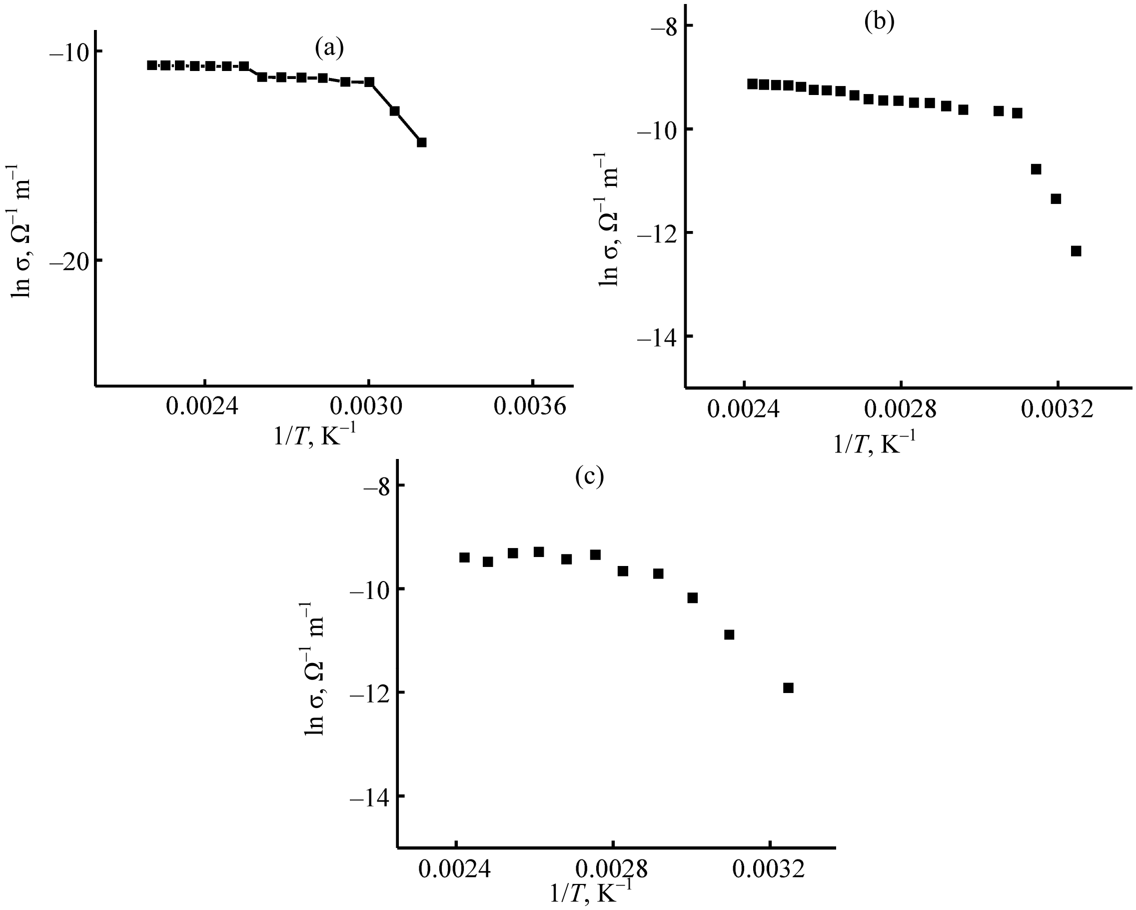

Fig. 1. AC conductivity at different temperature *T* (K) and frequency at 2 MHz for: (a) **I**, (b) **II**, and (c) **III** complexes.

trinitrophenol, PA) and 3,5-dinitrobenzoic acid (DNB) were prepared by mixing 1 mmol of the donor (Nor) in methanol (10ml) with 1 mmol of each acceptor in the same solvent with constant stirring for about 6 hrs. Solutions were allowed to slowly evaporate at room temperature, the solids precipitated were filtered off, washed several times with little amounts of solvent and dried under vacuum over anhydrous calcium chloride.

[(Nor)(PA)] (I) (yellow), $C_{22}H_{21}FN_6O_{10}$, M_W 548.40.

[(Nor)(DNB)] (II) (buff), $C_{23}H_{22}FN_5O_9$, M_W 531.42.

[(Cip)(PA)](III) (pale yellow solid), $C_{23}H_{21}FN_6O_{10}$, M_W 560.45.

Physical measurements. In this work AC Conductivity (σ) of disk shaped samples were measured, at room temperature from 323 to 583 K, over wide range of frequencies from 50 up to 5MHz. It is to mention that the measurements of dielectric properties (dielectric constant ε') were also performed on pressed disk samples of over the same range of temperature and frequency.

RESULTS AND DISCUSSION

AC conductivity as a function of temperature is shown in Fig. 1 at constant field frequency equal to 1 MHz. It can be noticed that the conductivity tends to increase slightly with increasing temperature. As shown in Figs. 1a–1c no significant trend of AC conductivity **I**, **II**, and **III** complexes was detected. The AC conductivity of all three complexes show semiconducting behavior. However, the activation energy of each complex is bit differ than the other. Table contains the activation energy values for the corresponding complex.

The activation energy ΔE was calculated according to equation:

$$\sigma_T = \sigma_0 e^{-\Delta E/K_B T}, \quad (1)$$

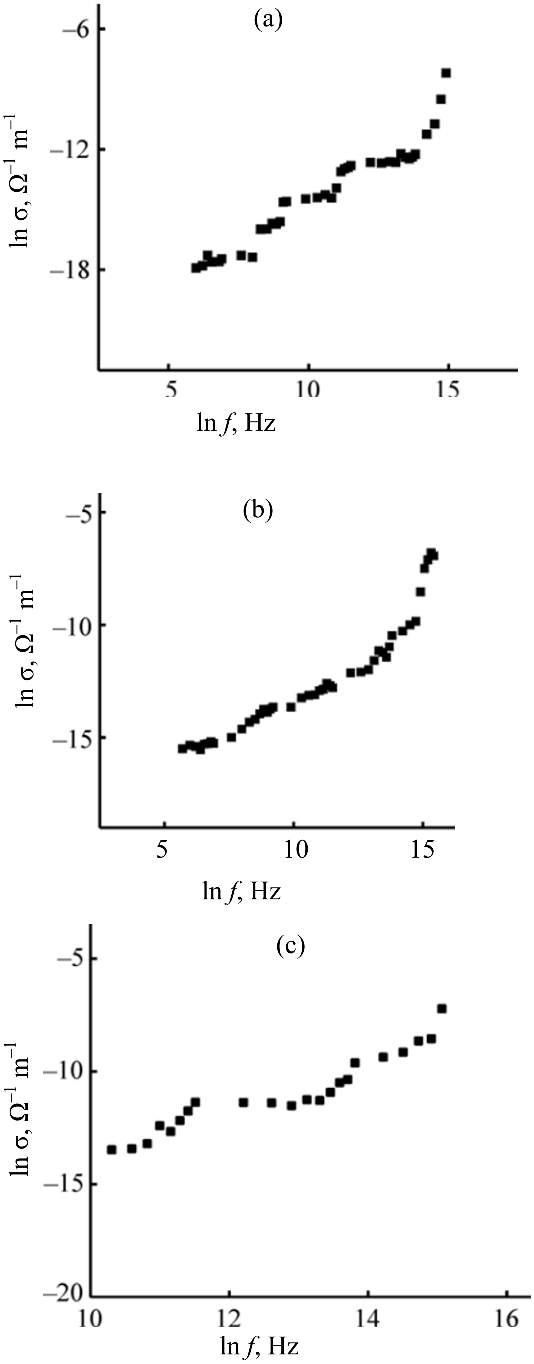

Fig. 2. Frequency dependence of AC conductivity at T = 323 K for (a) **I**, (b) **II,** and (c) **III** complexes.

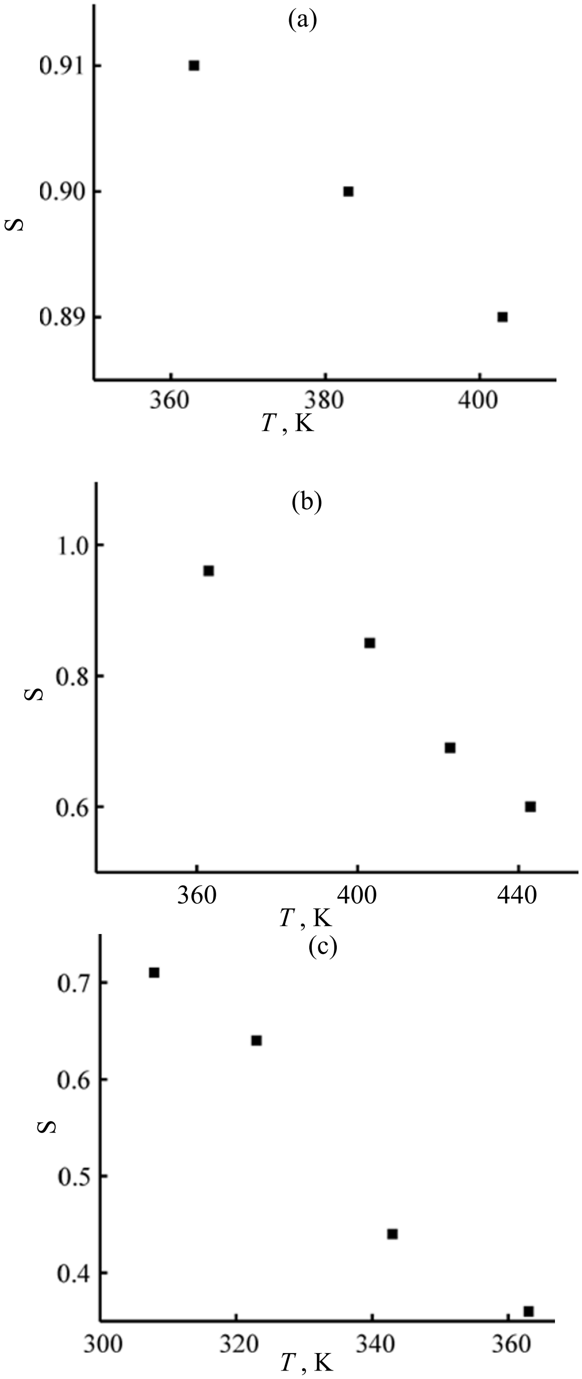

Fig. 3. Variation of the exponent factors against temperature for: (a) **I**, (b) **II,** and (c) **III** complexes.

where σ_T is the conductivity at temperature T and σ_0 is preexponential factor.

In the above equation K_B represents Boltzmann constant and T is the temperature in K. It can be observed that the activation thermal energy ΔE of the **II** is higher than that of **I** and **III**. In Fig. 1 for all three complexes, two distinct regions can be observed. Region 1, the low temperature region and the high temperature region, region 2. Such regions can be referred to many mechanisms. These mechanisms are the decomposition of the complex, the transition from the intrinsic semiconductor to an extrinsic semiconductor and phase change. For the frequency

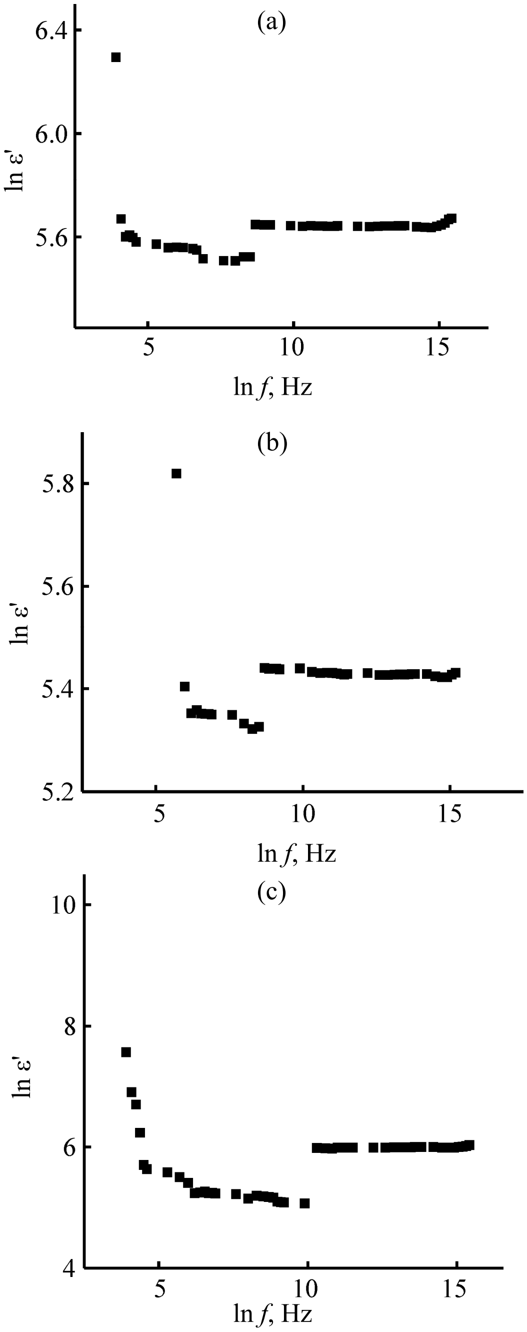

Fig. 4. Frequency dependence of dielectric constant (ε') at 323 K for: (a) **I**, (b) **II,** and (c) **III** complexes.

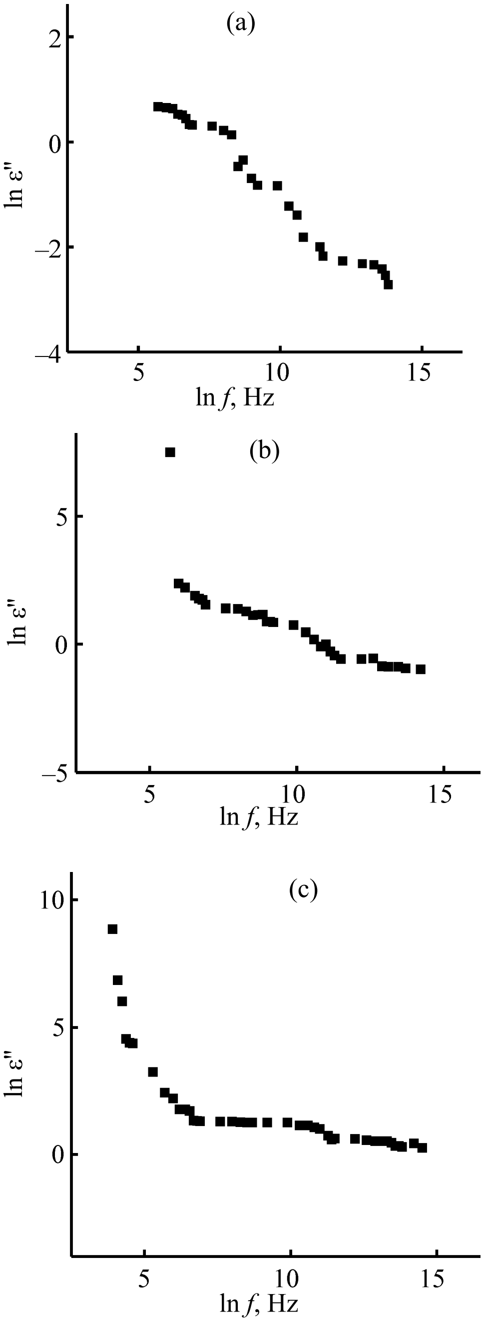

Fig. 5. Frequency dependence of dielectric loss (ε") at 323 K for : (a) **I**, (b) **II,** and (c) **III** complexes.

dependence of AC conductivity of the three complexes, an example for each complex at $T = 323$ K is shown in Figs. 2a–2c, the AC conductivity tends to increase slightly with increasing frequency. This can also be attributed to the enhancement of the conduction carriers by applied external field. The dispersion shown in Figs. 2a–2c. According to this dispersion the conductivity versus frequency verifies the following expression [24].

$$\sigma(\omega) = \sigma_{dc} + B\omega S, \qquad (2)$$

where σ(ω) is the AC conductivity, ω is the angular frequency which equals $\omega = 2\pi f$, S is frequency exponential factor and B is constant. The frequency

Activation energy, exponential factor and optical band gap for [(Nor)(PA)], [(Cip)(PA)], and [(Nor)(DNB)] complexes

Comp. no.	ΔE_1, eV at high tempature	ΔE_2, eV at low tempature	Exponential factor S	Optical band gap w_H, eV
I	0.03	0.29	0.700	0.55
II	0.08	0.68	0.780	0.76
III	0.03	0.58	0.713	0.58

exponential factor, S, can be obtained by plotting ln σ(ω) 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. Since the value of S decreases with the increasing of temperature as shown in Figs. 3a–3c, the conduction mechanism is considered to be due to correlation barrier hopping. According to this model S can be written as Eq. (3) [25]

$$S = 1 - (6K_BT/w_H), \tag{3}$$

where w_H is barrier height substitution for K_B, T, and S, w_H was calculated for each complex and recorded in the table.

Dielectric properties. For all three complexes, the dielectric constant and dielectric loss (ε' and ε'') were measured as a function of frequency of applied electric field at different temperatures.

It has been found that all three complexes have similar trend of the variation of the dielectric constant against frequency at different temperature. This dependence is depicted by Figs. 4a–4c where the dielectric constant tends to sharply decrease with the increasing of applied field frequency. In the range of high frequency the dielectric constant seems likely to be frequency independent. Such behavior can be attributed to polarization associated with the heterogenous structure. On the other hand, the frequency independence of the dielectric constant is due to the low charge carrier's mobility which hinders the frequency change and cannot follow the frequency change.

Figures 5a–5c represents the frequency dependence of the dielectric loss ε'' at temperature equal to 323 K. It is noticed that the dielectric loss of **I, II**, and **III** is continuously decreasing with frequency in the studied range of frequencies.

CONCLUSIONS

(1) Semiconductor behavior was observed for all three studied complexes.

(2) Regarding the activation energy for the studied complexes, the activation thermal energy ΔE of **II** is higher than that for **I** and **III**.

(3) In addition, the conduction mechanism in the three studied complexes is considered to be due to correlation barrier hopping.

(4) The dielectric constants of **I**, **II,** and **III** are relatively high, of value about 250.

(5) At low frequency, the dielectric constant of all studied complexes tend to decrease sharply, may be due to the polarization resulting from the heterogeneous structure.

(6) The dielectric constant of **I**, **II,** and **III** seem to be frequency independent at high frequency, that may be attributed to low mobility of charge carriers which can not follow the applied field.

(7) It is noticed that the dielectric loss of all three complexes is continuously decreasing with frequency in the range of studied frequency.

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