Dielectric, Electrical Conductivity Behavior and Molecular Modeling of Some Pyrimidine and Purine Compounds

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Citation: *MS Masoud, M Sh Ramadan, AM Sweyllam and MH Al-Saify (2021) Dielectric, Electrical Conductivity Behavior and Molecular Modeling of Some Pyrimidine and Purine Compounds. J Chem Edu Res Prac 5: 64-88.*

Abstract
The dielectric and electrical conductivity measurements for biologically active nucleic acid compounds reveal semiconducting properties and small relaxation times. On the basis of electronic transition within molecules, two pathways for the conduction of electricity may be expected. The first conducting process occurring in the lower temperature region is attributed to $n\rightarrow\pi^*$ transitions which require less energy to be performed. In the upper temperature region, conduction could be attributed to $\pi\rightarrow\pi^*$ transitions which need more energy to participate in electronic conduction. The observed increment of conduction in the upper temperature region may be attributed to interactions between $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular orbital energy (E_{LUMO}) were given using molecular modeling. Energy gap (ΔE) and parameters which give information about the reactive chemical behavior of compounds such as electronegativity (χ), chemical potential (μ), global hardness (η), softness (σ) and electrophilicity index (ω) were calculated.

Keywords: Dielectric, Electrical Conductivity, Capacitance (Cp), Loss Tangent (tan δ), Cole-Cole Diagram, Relaxation Time (τ), Activation Energy, Molecular Modeling

Introduction

Dielectric measurements are important methods for studying the dynamic properties (capacitance, impedence, permittivity and loss factor) of dielectrics. This behavior was associated with a hopping mechanism in terms of correlated barrier hopping (CBH) model for alternating current (a.c.) loss, first developed by Pike for single-electron hopping, and has been extended by Elliot for simultaneous two electrons hopping [1, 2].

The dielectric relaxation studies are important to understand the nature and the origin of dielectric losses, which in turn, may be useful in the determination of the structure and defects in solids [3-7].

In recent years, the study of the electrical conduction mechanism in organic compounds has been the subject of many theoretical and experimental investigations. The interest of this topic is stimulated by the applications of these compounds in the development of various modern and future technologies of solid-state devices. Moreover, the information about the electrical properties of mate-

rials is also necessary for determining the optimum conditions and analysis of electrical transport in these materials. Also, both direct current(d.c.) and alternating current(a.c.) measurments provide important information about the conduction process and the predominant charge transport mechanism within an organic material [7].

Organic semiconductors are of steadily growing interest as active components in electronics and opto-electronics. Due to their flexibility, low cost and ease of production they represent a valid alternative to conventional inorganic semiconductor technology [8].

The increasing environmental consciousness throughout the world has triggered a search for new products and processes that are compatible with the environment.

Experimental
Synthesis of Metal Complexes in The Solid State
These were prepared by mixing metal chloride solutions with li-

gand solutions, Table (1), hence they were refluxed, filtered and dried for the separated products. The metal ions were determined by atomic absorption techniques and complexometric titrations using published procedures [9]. The complexes were digested by aqua regia several times to complete decomposition for the organic ligand compounds. The analyzed complexes were given in Table (2a-b).
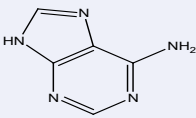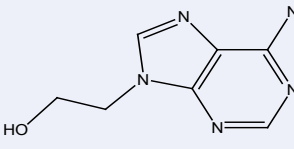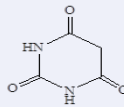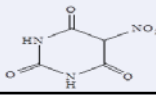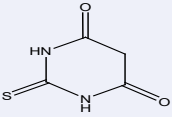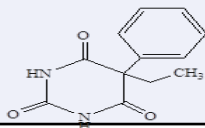
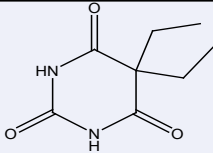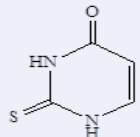## Instruments and Working Procedures
Dielectric and Electrical Conductivity Measurements
1. Four test parameters including impedance |Z|, phase angle θ, parallel equivalent static capacitance Cp and loss tangent tan δ were measured for the ligands and complexes in the solid state at constant voltage 0.80 volt but different temperatures (40-240°C) and at variable frequencies (500 Hz - 5 MHz) using HIOKI "3532-50 LCR HITESTER" instrument.

2. The ligands and complexes were prepared in the form of tablets at a pressure of 6-7 tons/cm^2 with 10 mm diameter and 0.7-4.4 mm thickness. Silver metal was evaporized on the major faces of each test piece to improve the contact with the measuring electrodes. The tablets were hold between two copper electrodes and then inserted with the holder vertically into cylindrical electric furnace. The potential drop across the heater was varied gradually through variable transformer to produce slow rate of increasing the temperature to get accurate temperature measurements using a pre-calibrated Cu-constantan thermocouple attached to the sample.

3. The dielectric constant ε, the dielectric loss ε´´, real part of impedance Z´, imaginary part Z´´, the conductivities $\sigma_{a.c}$. (a.c.: alternating current condition), the relaxation times τ_o, τ and the activation energies ΔE of the ligands and complexes were calculated [10].

Molecular Modeling
The ChemOffice Ultra 2004 computer and HyberChem programs are used for molecular modeling studies of the ligands and their complexes.

Table 1: Names, abbreviations, m.p. and structures of the ligands are given*.

Compound	Abbreviation	M.P.°C	Structures
Adenine	(AD)	360-365	
9-Hydroxyethyladenine	(HEAD)	244	
Barbituric acid	(BA)	248	
5-Nitrobarbituric acid	(NBA)	176	
Thiobarbituric acid	(TBA)	245	
Phenobarbital	(PB)	174-178	

Barbital	(B)	190	
2-Thiouracil	(TU)	340	

Cont.

* All these ligands are of white colour except TBA is of yellow colour and were purchased from BDH company.

Table 2a: C, H, N, S elemental analysis for some nucleic acid constituent complexes.

Complex	Colour	Formula	Calculated/(Found) %			
			C	H	N	S
Co-Ni(TU)$_3$.4H$_2$O	brown	C$_{12}$H$_{16}$N$_6$O$_7$S$_3$CoNi	25.28	2.83	14.74	16.87
			(25.00)	(2.80)	(15.20)	(17.00)
Hg(BA)$_2$	buff	C$_8$H$_6$N$_4$O$_6$Hg	21.13	1.33	12.32	-
			(21.60)	(1.52)	(12.51)	(-)

Table 2b: H, N, S, M elemental analysis for some nucleic acid constituent complexes.

| Complex	Colour	Formula	Calculated/(Found) %			
			H	N	S	M
Cr(TU)(OH$^-$)$_2$.H$_2$O	green	C$_4$H$_7$N$_2$O$_4$SCr	3.05	12.12	13.87	22.49
			(3.32)	(12.50)	(14.00)	(22.66)
Mn(TU)$_2$.H$_2$O	brown	C$_{16}$H$_{16}$N$_8$O$_5$S$_4$Mn	2.76	19.21	21.98	9.41
			(3.00)	(20.00)	(22.00)	(9.88)
Hg(TU)$_2$.4H$_2$O	white	C$_8$H$_{14}$N$_4$O$_6$S$_2$Hg	2.68	10.63	12.17	38.07
			(3.00)	(11.00)	(12.00)	(38.12)

Results and Discussion
Dielectric and Electrical Conductivity Measurements
Dielectric Measurements

A dielectric materials measurement can provide critical design parameter information for many electronics applications. For example, the loss of a cable insulator, the impedance of a substrate, or the frequency of a dielectric resonator can be related to its dielectric properties. The information is also useful for improving ferrite, absorber, and packaging designs. More recent applications in the area of industrial microwave processing of food, rubber, plastic and ceramics have also been found to benefit from knowledge of dielectric properties.

The dielectric behaviors of materials under external (a.c.) field have high scientific and technological importances. In polar dielectrics, the molecules, which are normally composed of two or more different atoms, have dipole moments even in the absence of an electric field, that is, the centres of their positive and negative charges do not coincide [11]. Normally the molecular dipoles are randomly oriented throughout the material owing to thermal agitation, so that the average moment over any macroscopic volume element is zero. In the presence of an externally applied field, the molecules tend to orient themselves in the direction of the field as shown in the following diagram:

Unpolarized

Polarized by applied electric field
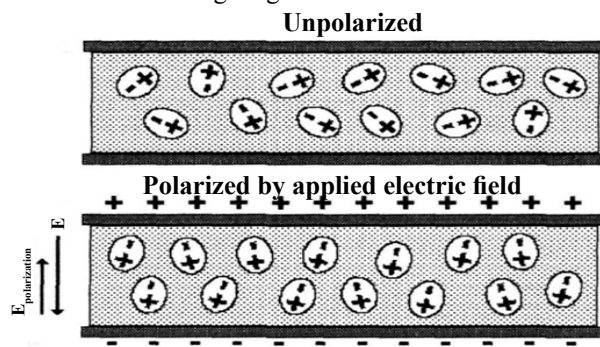
For a parallel-plate condenser in which a dielectric tablet fills the

space between the plates, the capacitance is given by [12]:

$C_p = A\varepsilon\varepsilon_o / d$

Where ε_o is the permittivity of a vacuum and its value is approximately 8.854×10^{-12} F m^{-1}, ε is the dielectric constant of a dielectric, A and d are the area and the thickness of the matter tablet, respectively.

The complex dielectric permittivity, $\varepsilon^*(\omega)$ is given as follows [13]:

$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the complex permittivity, respectively. ω is the angular frequency, $\omega = 2\pi f$ and $i = \sqrt{-1}$.

$\varepsilon'(\omega) = \varepsilon \sin\theta$, $\varepsilon''(\omega) = \varepsilon \cos\theta$

where θ is the phase shift.

The loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$, $\delta = 90°-\theta$

The real and imaginary parts of the complex impedance are given by:

$Z' = Z \cos\theta$, $Z'' = Z \sin\theta$

where Z' and Z" are the real and imaginary parts of the impedance, respectively.

Dispersion arising during the transition from full orientational polarization at zero or low frequencies to negligible orientational polarization at high radio frequencies is referred to as dielectric relaxation [14].

The rate of decay and build-up of the orientational polarization, as given by the relaxation time τ, will depend upon the thermal energy of the dipoles as well as upon the internal or molecular friction forces encountered by the rotating dipoles.

The dielectric parameters for the investigated ligands and complexes are illustrated in terms of temperature and frequency (ln f) changes, Figures (1-12). The more spotlight points, could be given as follows:

1. The capacitance (C_p) decreases with increasing the applied frequency in some different ranges which may be attributed to the effect of charge redistribution by carrier hopping on defects [15, 16]. At low frequency, the charge on defects can be rapidly redistributed so that defects closer to the positive side of the applied field become negatively charged, while defects closer to the negative side of the applied field become positively charged. This leads to screening of the field and an overall reduction in the electric field. Because capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed as the frequency is lowered. In case of high frequency, the defects no longer have enough time to rearrange in response to the applied voltage, hence the capacitance decreases.

2. ε' and ε'' decrease with increasing frequency (ln f), which can be explained as follows:
    (a) At low frequencies the dielectric constant for polar materials is due to the contribution of multi-component of polarizability, deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization) [17].

(b) When the frequency begins to increase, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation polarization stopped, so ε' and ε'' decrease at higher frequencies approaching a constant value due to the interfacial or space charge polarization only [4, 18].

3. The relative permittivity and dielectric loss values for the complexes, Figures (8-12), reveal semiconducting features based mainly on the hopping mechanism [19].

4. The loss tangent (tan δ) is decreased with increasing frequency, while at certain temperatures for ligands(HEAD, NBA) and complexes(Cr(TU)(OH$^-$)$_2$.H$_2$O, Mn(TU)$_2$.H$_2$O, Co-Ni(TU)$_3$.4H$_2$O, Hg(TU)$_2$.4H$_2$O) a well-defined peaks are observed corresponding to dielectric relaxation phenomena, Figures (2, 4, 9-12) [20].

5. The impedance (Z) is mostly decreased with increasing frequency, Figures (1-12). The Z"-Z' relationships are illustrated in Figures (13, 14) at different temperatures.
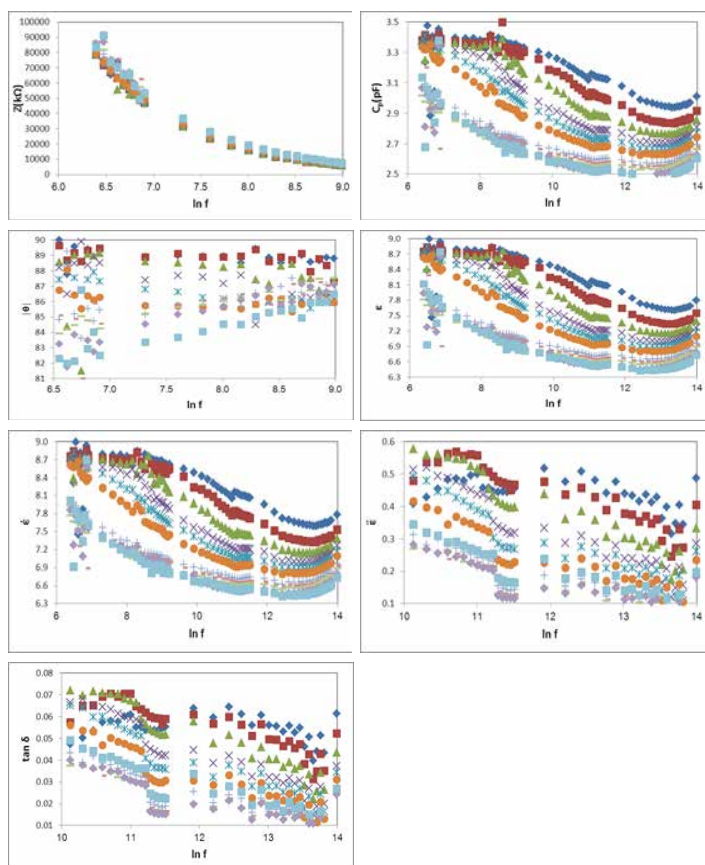

Figure 1: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′,ε″, tan δ) - lnf relationships for AD at different temperatures 40°C, 60°C, 80°C, 100°C, 120°C, 140°C, 160°C, 180°C, 200°C, 220°C and 240°C
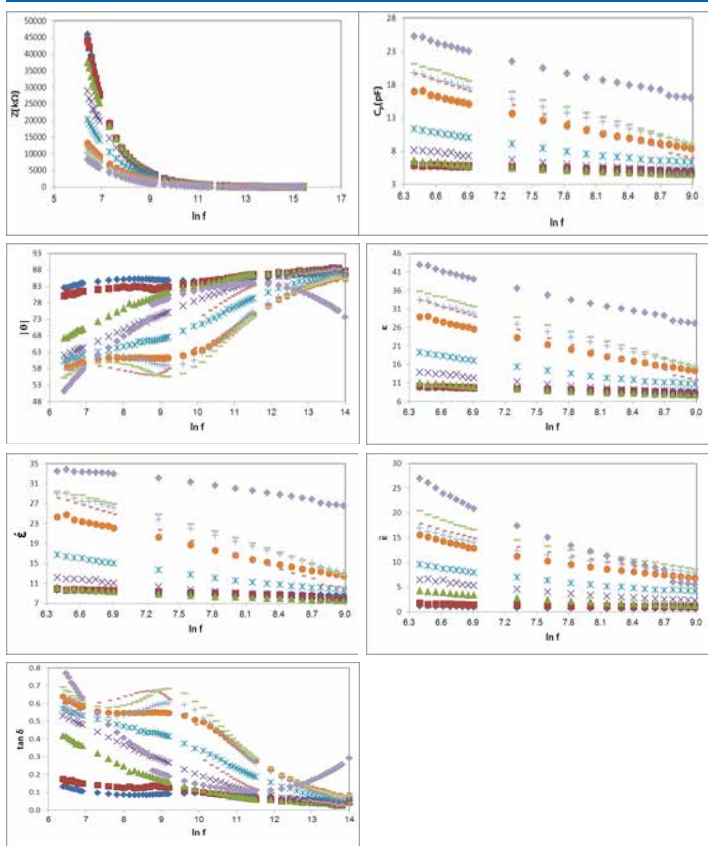
Figure 2: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for HEAD at different temperatures ◆40°C,■60°C, ▲80°C,✕100°C,✳120°C,●140°C,+160°C,▬180°C, 200°C and ●220°C
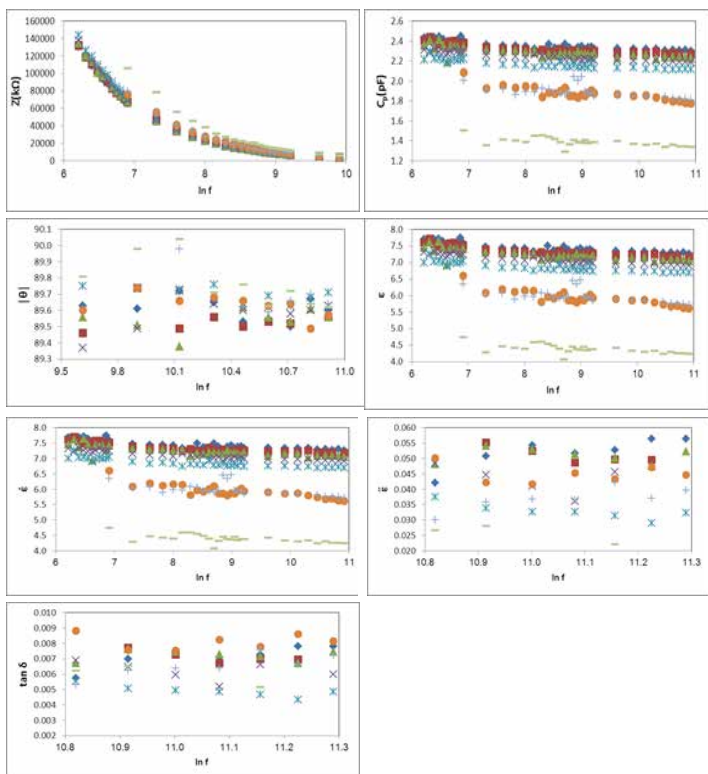
lnf relationships for TBA at different temperatures ◆40°C,■60°C, ▲80°C,✕100°C,✳120°C,●140°C,+160°C,▬180°C and ▬200°C
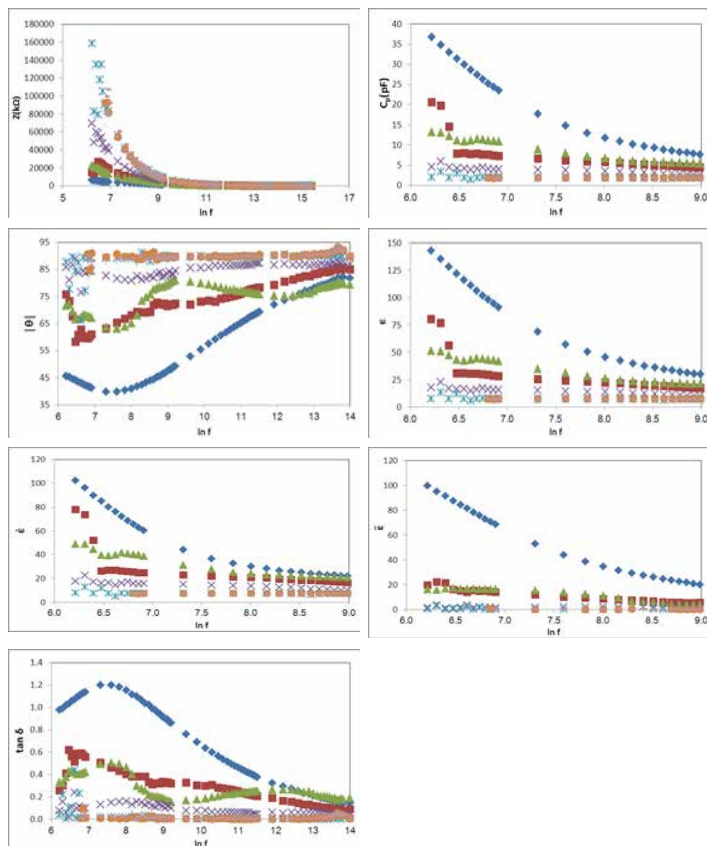
Figure 4: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ)-lnf relationships for NBA at different temperatures ◆40°C,■60°C, ▲80°C,✕100°C,✳120°C,●140°C,+160°C and ▬170°C

Figure 3: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ) -
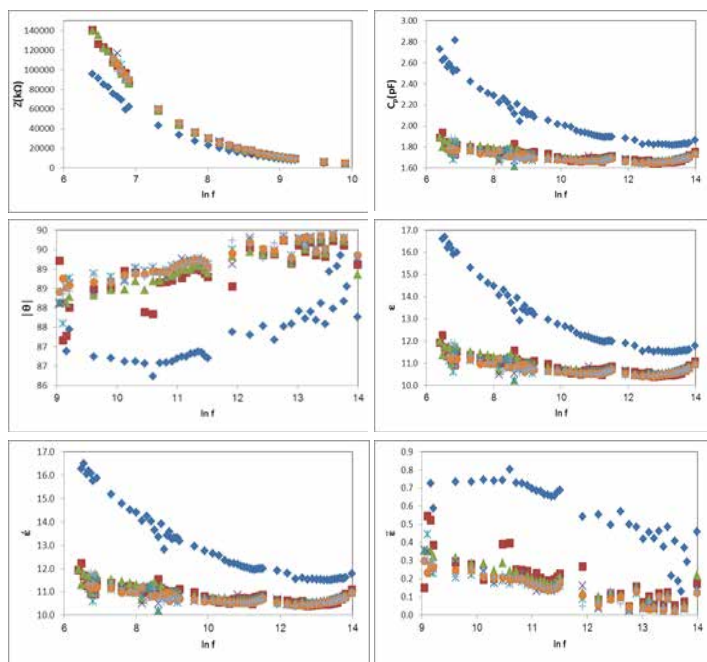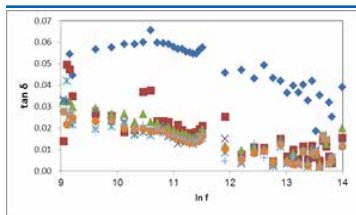
Figure 5: The dielectric parameters (Z, C_p, |θ|, ε, ε′, ε″, tan δ)- lnf relationships for B at different temperatures ◆40°C, ■60°C, ▲80°C, ✕100°C, ✳120°C, ●140°C and ╋160°C

Figure 7: The dielectric parameters (Z, C_p, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for TU at different temperatures ◆40°C, ■60°C, ▲80°C, ✕100°C, ✳120°C, ●140°C, ╋160°C, ▨180°C, ▬200°C, ●220°C and ■240°C
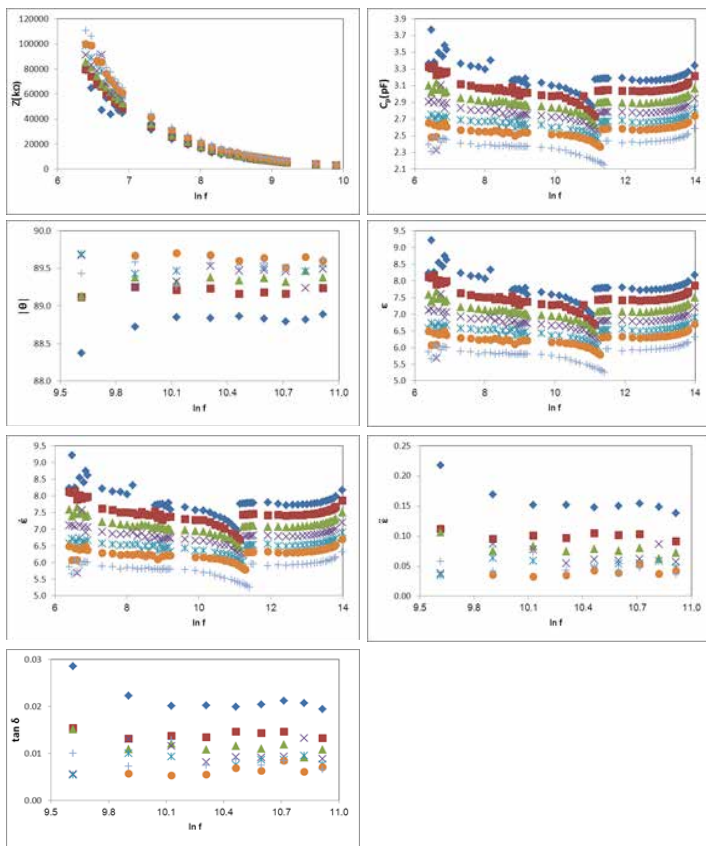
Figure 6: The dielectric parameters (Z, C_p, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for PB at different temperatures ◆40°C, ■60°C, ▲80°C, ✕100°C, ✳120°C, ●140°C and ╋150°C
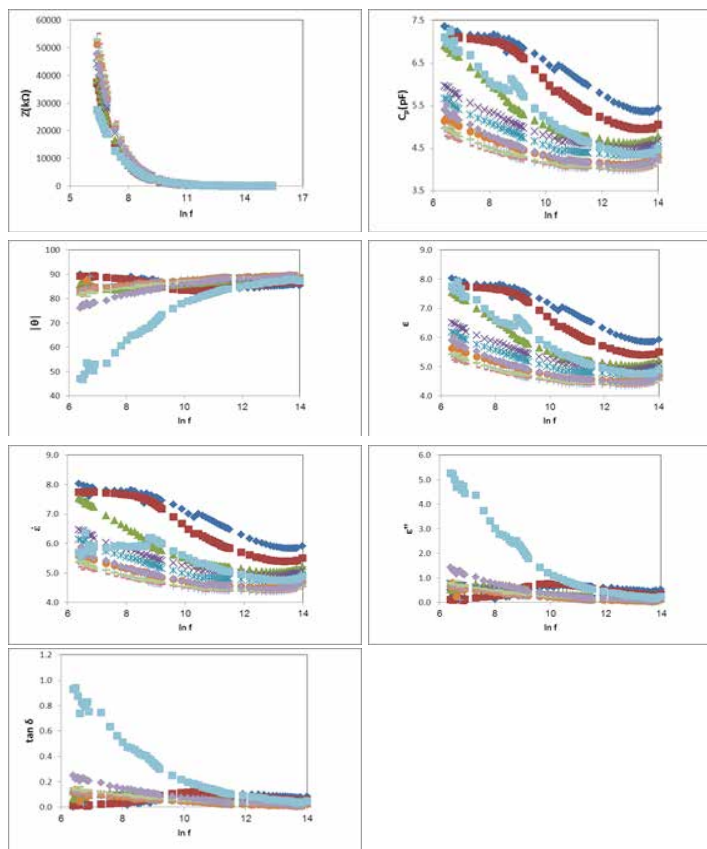
Figure 8: The dielectric parameters (Z, C_p, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for Hg(BA)$_2$ at different temperatures ◆40°C, ■60°C, ▲80°C, ✕100°C, ✳120°C, ●140°C, ╋160°C, ▨180°C, ▬200°C, ●220°C and 240°C
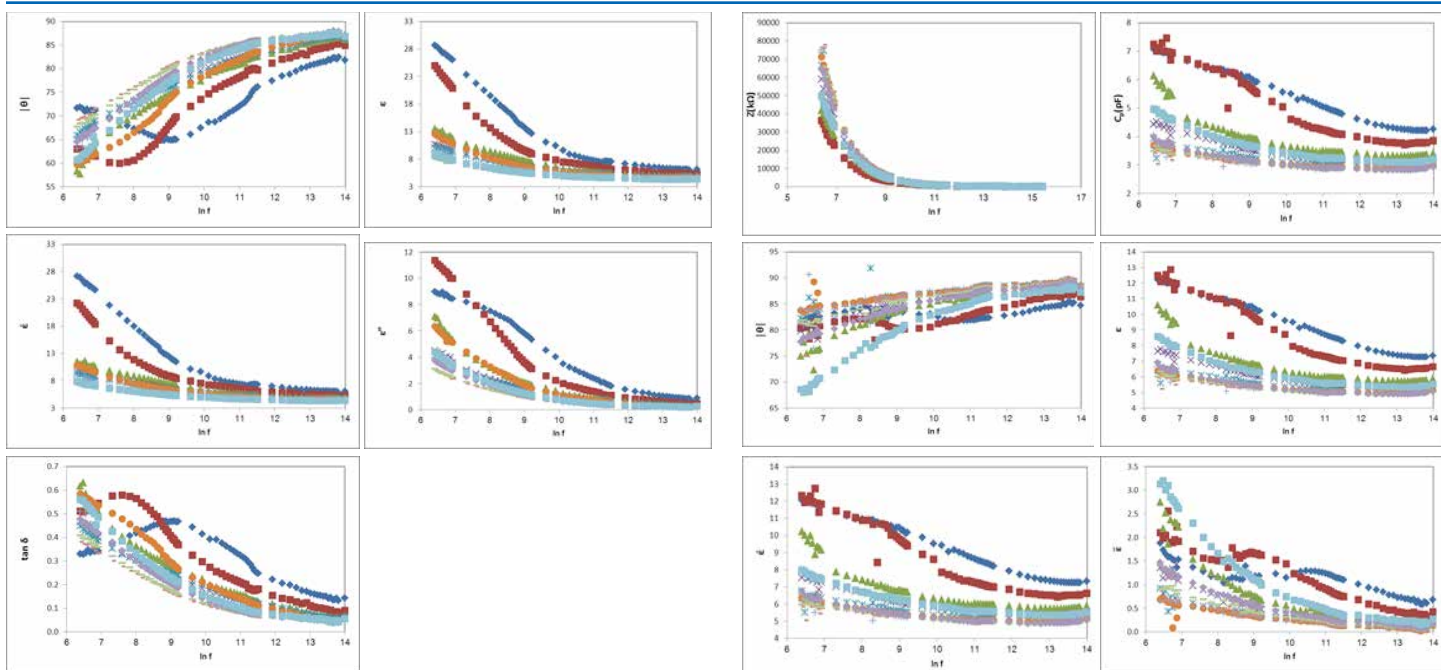
Figure 9: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ)-lnf relationships for Cr(TU)(OH$^-$)$_2$.H$_2$O at different temperatures ◆40°C,■60°C,▲80°C,×100°C,×120°C,●140°C,+160°C,▬180°C,▬200°C, ◆220°Cand ▬240°C.
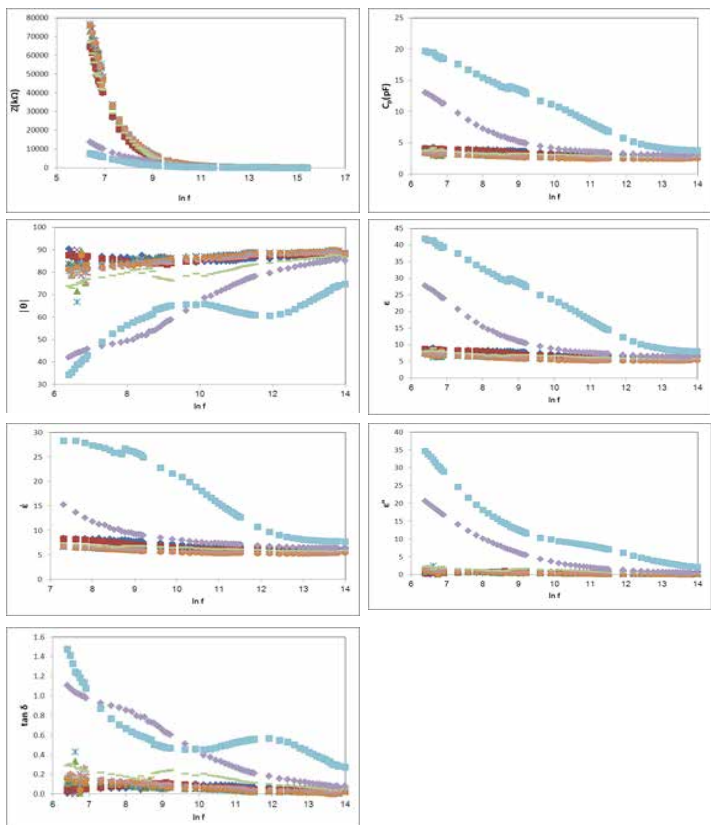
Figure 10: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for Mn(TU)$_2$.H$_2$O at different temperatures ◆40°C,■60°C,▲80°C,×100°C×120°C,●140°C,+160°C,▬180°C,▬200°C, ◆220°Cand■240°C
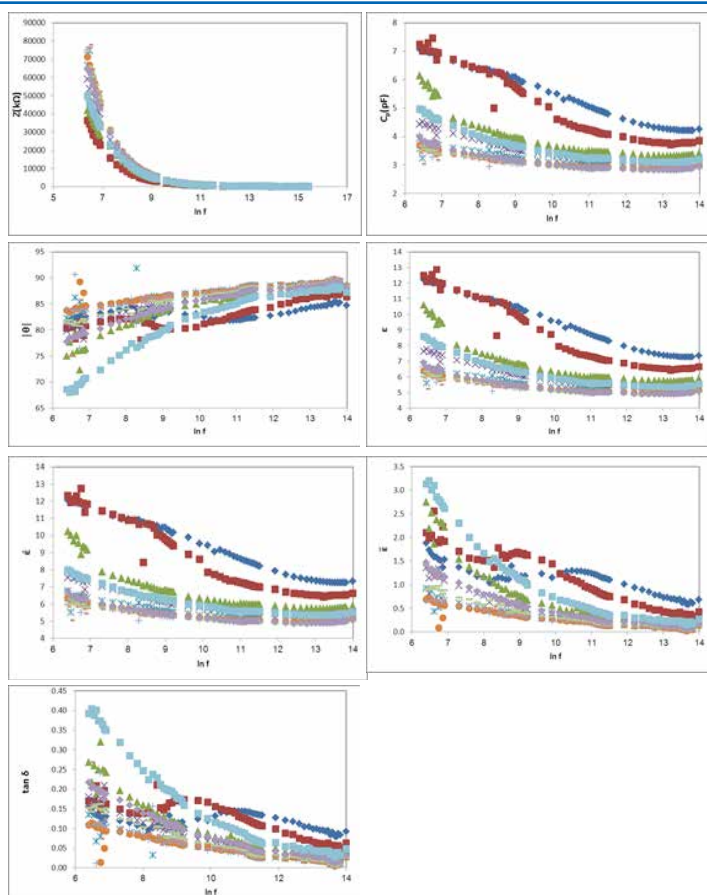
Figure 11: The dielectric parameters (Z, C$_p$, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for Co-Ni(TU)$_3$.4H$_2$O at different temperatures ◆40°C,■60°C, ▲80°C,×100°C,×120°C,●140°C,+160°C,▬180°C,▬200°C, ◆220°Cand ■240°C
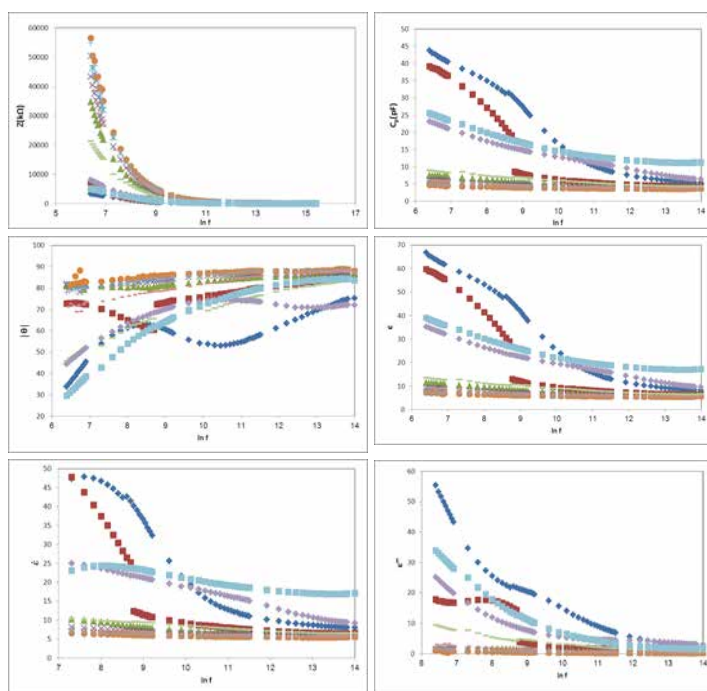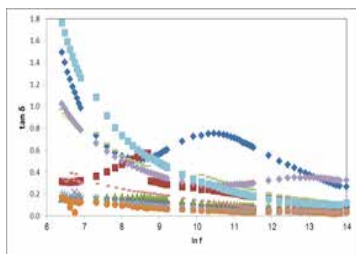
Figure 12: The dielectric parameters (Z, C_p, |θ|, ε, ε′, ε″, tan δ) - lnf relationships for Hg(TU)₂.4H₂O at different temperatures ◆40°C,■60°C,▲80°C,✕100°C,✕120°C,●140°C,+160°C,▬180°C,▬200°C,◆220°Cand■240°C
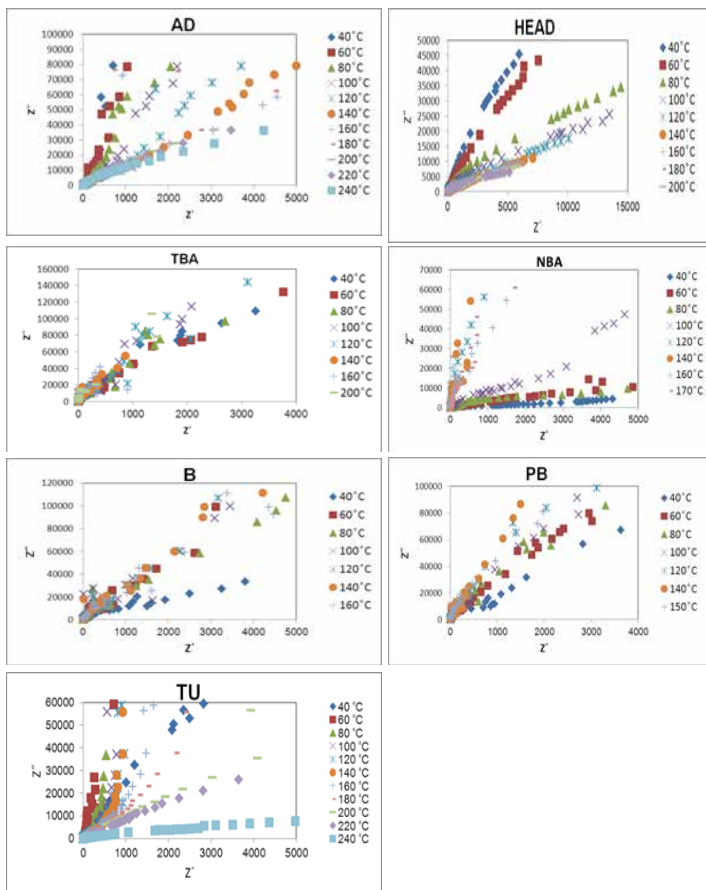
Figure 13: Z″-Z′ relationship for ligands at different temperatures
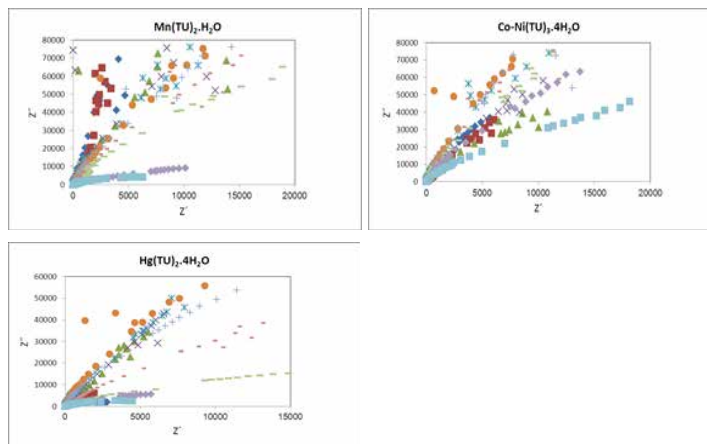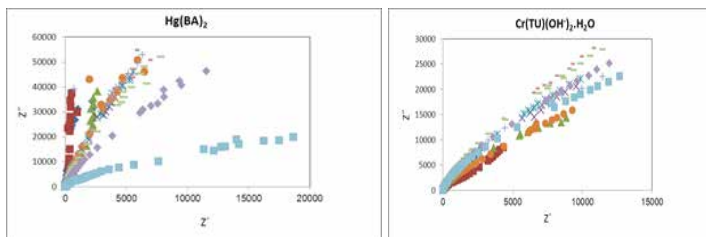
Figure 14: Z″-Z′ relationship for complexes at different temperatures ◆40°C,■60°C,▲80°C,✕100°C,✕120°C,●140°C,+160°C,▬180°C,▬200°C, and■240°C

The evaluation of experimental dielectric data is much facilitated by certain graphical methods of display, which permit the derivation of parameters by geometrical construction. The earliest and most used of these methods consists of plotting the imaginary part ε′(ω) for a certain frequency against the real part ε″(ω) at the same frequency, in cartesian coordinates or in the complex plane [21]. This diagram may be called the complex locus diagram or Argand diagram and was applied to dielectrics by Cole and Cole, illustrated in a familiar plot or arc plot [22].

For a dielectric with a single relaxation time the Cole-Cole plot is a semi-circle which provides an elegant method of finding out whether a system has a single relaxation time or more. The arc plot of a dielectric with a single relaxation time is illustrated in Figure (15(a) and (b)).
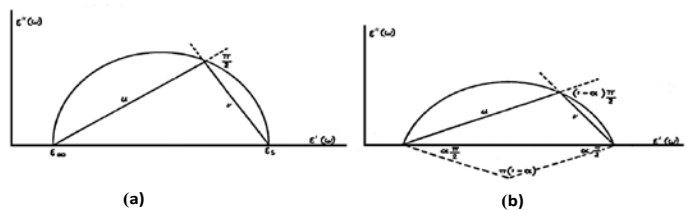
Figure 15: (a) Arc plot for a Debye dielectric; (b) Arc plot for a dielectric with a Cole-Cole distribution characterized by the parameter α (from Cole and Cole) [22].

For polar compounds, a semi-circle is obtained on plotting ε″(ω) against ε″(ω) for each temperature [23]. A given point on the semi-circle corresponds to a given frequency while the summit corresponds to ωτ = 1, Figure (15(a and b)). The plot has the disadvantage that ω does not appear in it. This semi-circle Cole-Cole diagram has been used to determine the distribution parameter α, which measures the width of distribution of relaxation time. Also, the macroscopic relaxation time τ_o and the molecular relaxation time τ can be determined [17, 22]. α values are evaluated by mea-

suring the angle between the real part of dielectric constant and radius of the circle.

If the centres of semi-circles lie ε'(ω) axis, α is zero (Debye type). Otherwise, the centre is below ε'(ω) axis and α ≠ 0 (non-Debye type) [24]. Two intersections between the real axis ε'(ω) and the circular arc, give the relative permittivity at zero frequency (static dielectric constant ε_s) and that at infinite frequency approaching the frequencies of light oscillators (optical dielectric constant ε_∞) [17]. A point on the semi-circle defines two vectors u and v, Figure (15 (a and b)), v is the distance on the Cole-Cole diagram between the static dielectric constant ε_s and the experimental point, u is the distance between that point and the optical dielectric constant ε_∞. Cole and Cole generalized the representation of a Debye dielectric by a circular arc plot in the complex plane so that it is applied to a certain type of distributions of relaxation times, so

$$v/u = (\omega\tau_o)^{1-\alpha}$$

where ω is the angular frequency. The parameter α equals zero when the compound has only one relaxation time, whereas for a series of relaxation times, the value of α varies between 0 and 1. The extent of the distribution of relaxation times increases with increasing parameter α. On the other hand, the value of τ_o decreases with increasing temperature [22]. The molecular relaxation time τ could be determined based on the following equation [22]:

$$\tau = \frac{2\varepsilon_s + \varepsilon_\infty}{3\varepsilon_s} \tau_o$$

The relaxation time is interpreted as the average time which a molecule spends in one of the equilibrium positions before jumping to the other one. The temperature dependence of τ can be expressed for thermally activated processes as [17]:

$$\tau = \tau_o e^{E_o/kT}$$

where τ_o is a constant characteristic relaxation time and represents the time of a single oscillation of a dipole in a potential well, E_o is the energy of activation for the relaxation of the dipole, k is the Boltzmann constant and τ represents the average or most probable value of the spread of the relaxation times. The Cole-Cole diagrams for the investigated ligands and complexes at different temperatures, Figures (16-27), reveal mainly non-Debye type [24].

The dielectric data obtained from the analysis of Cole-Cole diagrams for different ligands and complexes are collected in Table (3).

One must focus the attention that the molecular orientation and the association in molecular structure are important.

The variation of ln τ as a function of reciprocal absolute temperature for different ligands and complexes, Figures (28, 29), assigned that as the temperature increases, the relaxation time for each relaxator becomes smaller in some ranges.

The activation energies for the relaxation processes of different ligands and complexes are given in Table (4).
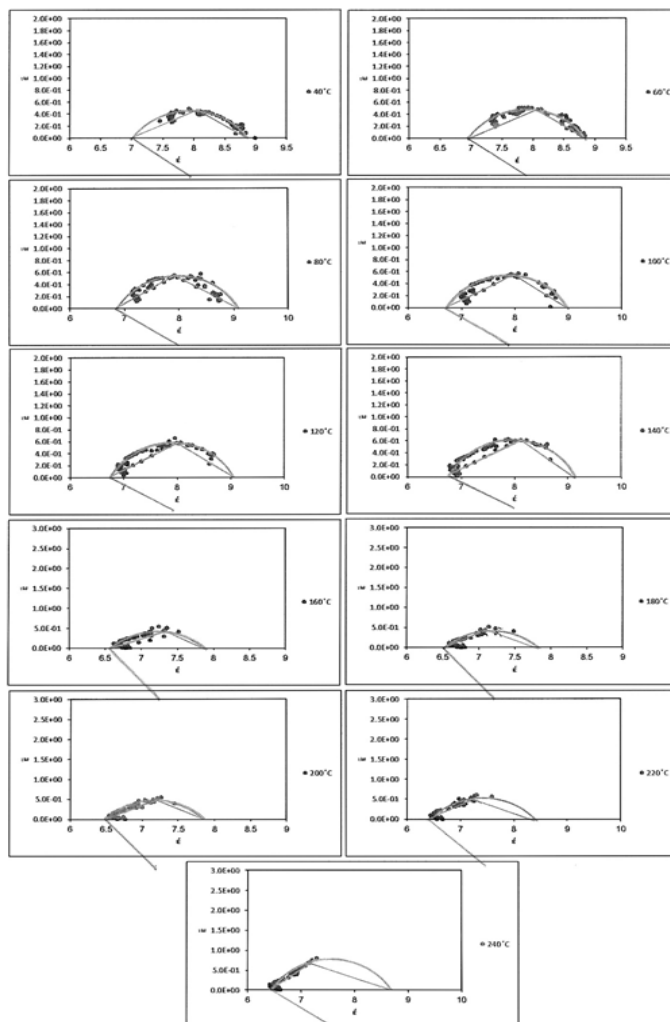
Figure 16: Cole-Cole diagrams for AD at different temperatures

Figure 17: Cole-Cole diagrams for HEAD at different temperatures
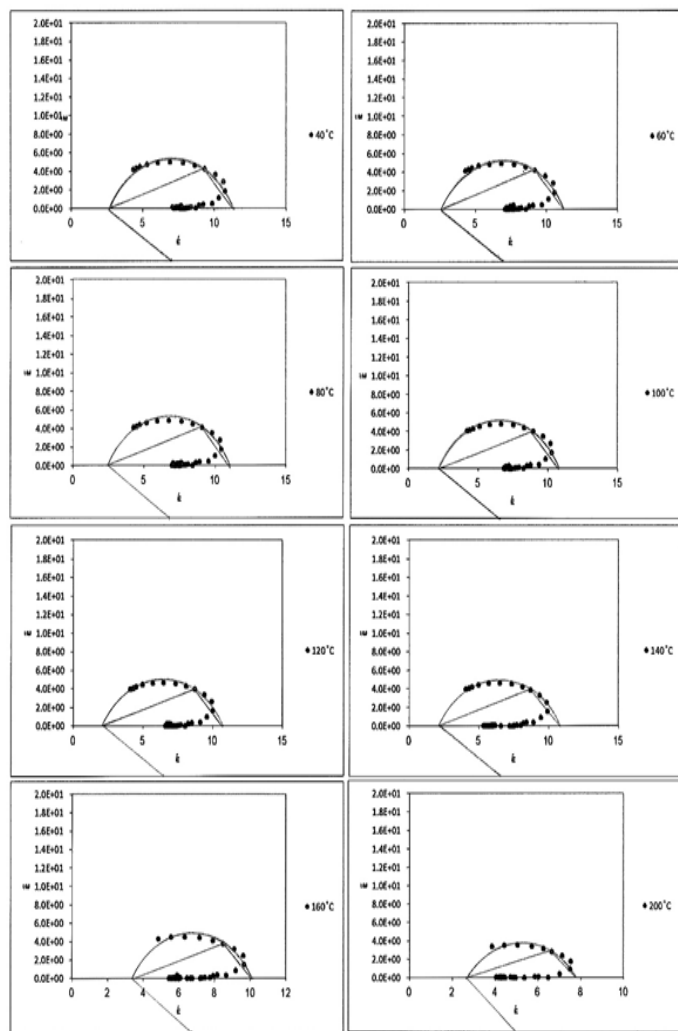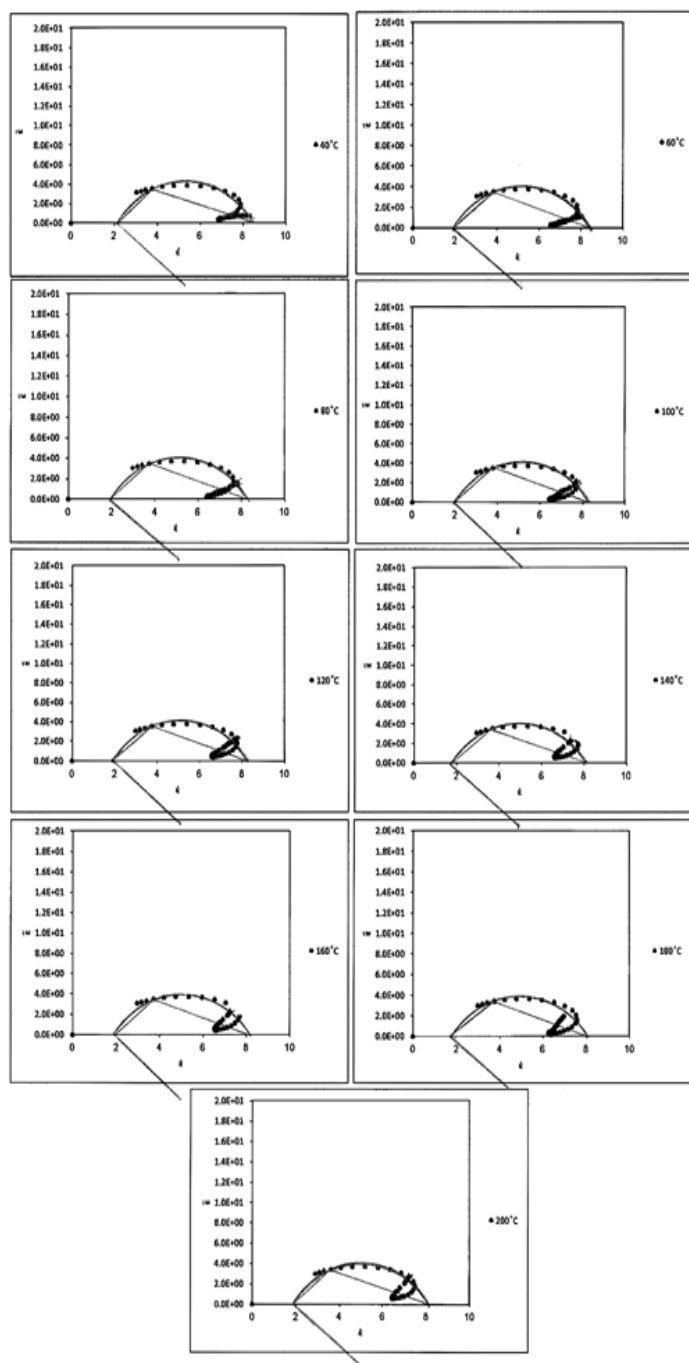
Figure 18: Cole-Cole diagrams for TBA at different temperatures
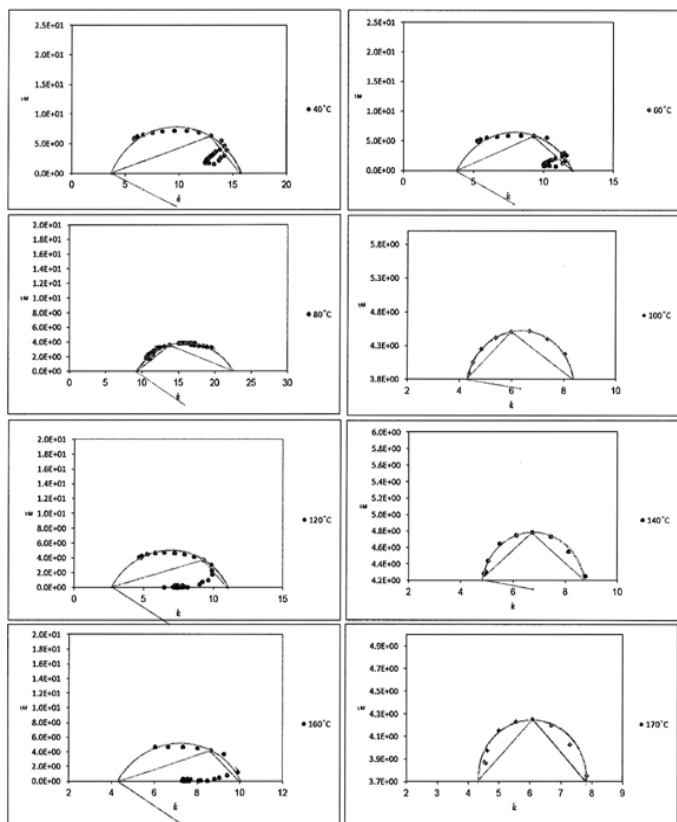
Figure 19: Cole-Cole diagrams for NBA at different temperatures

Figure 21: Cole-Cole diagrams for PB at different temperatures

Figure 20: Cole-Cole diagrams for B at different temperatures
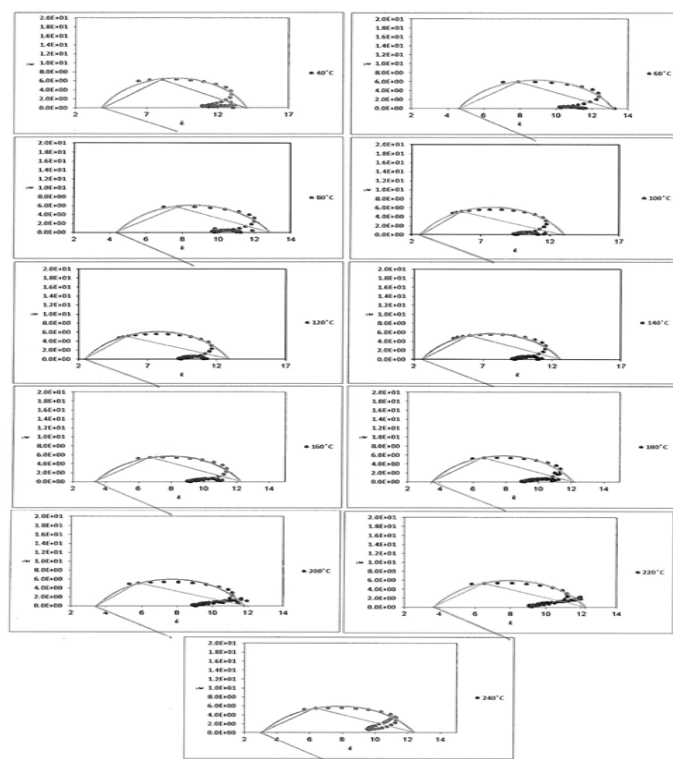
Figure 22: Cole-Cole diagrams for TU at different temperatures
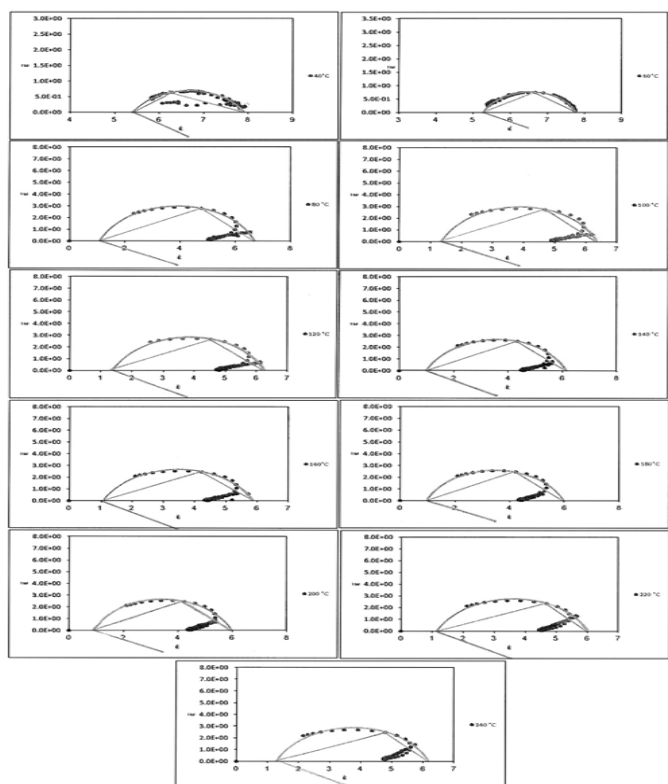
Figure 23: Cole-Cole diagrams for Hg(BA)$_2$ at different temperatures

Figure 25: Cole-Cole diagrams for Mn(TU)$_2$.H$_2$O at different temperatures

Figure 24: Cole-Cole diagrams for Cr(TU)(OH$^-$)$_2$.H$_2$O at different
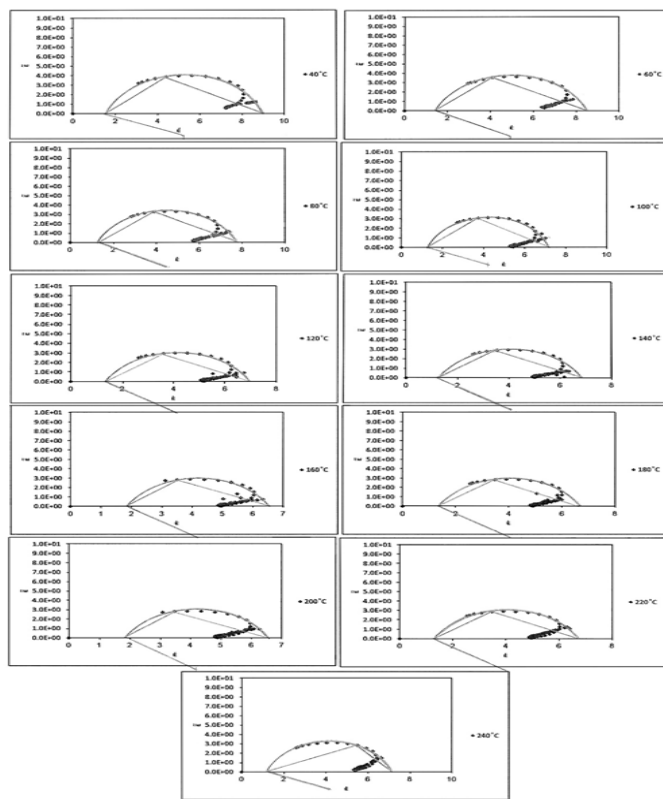
Figure 26: Cole-Cole diagrams for Co-Ni(TU)$_3$.4H$_2$O at different temperatures
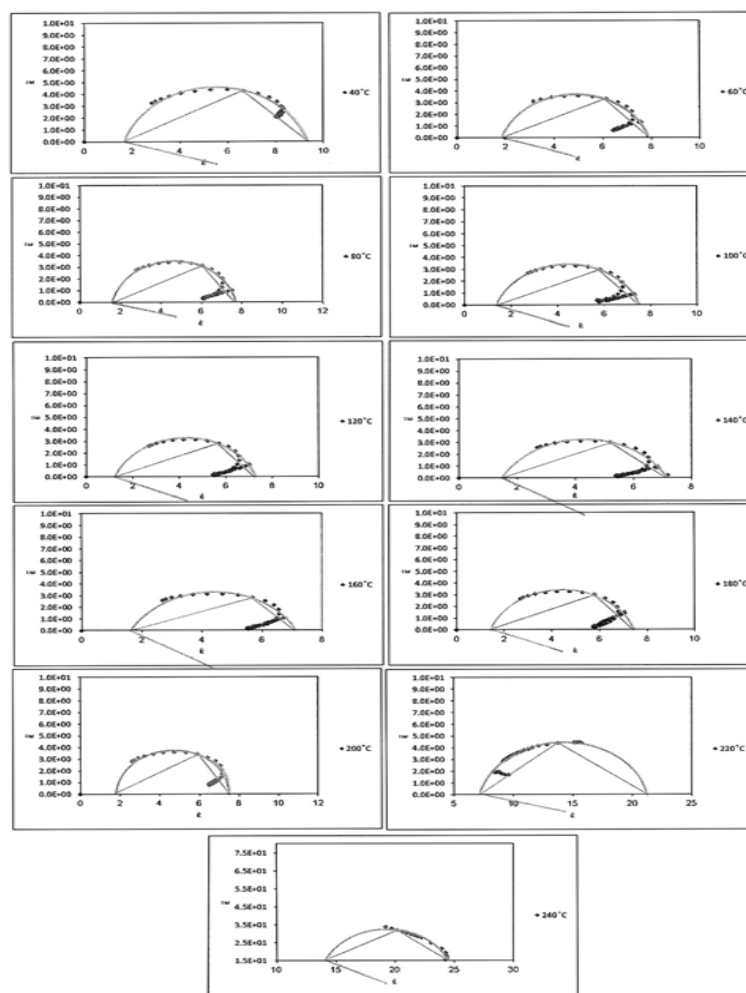
Figure 27: Cole-Cole diagrams for Hg(TU)$_2$.4H$_2$O at different temperatures

Table 3: The dielectric data obtained from the analysis of Cole-Cole diagrams for different compounds

Com- pound	Tem- perature (K)	ω	v	u	α π/2	α	1 - α	τ$_o$	ε$_s$	ε$_\infty$	τ	ln τ
AD	313	345575.2	1.20	1.40	35	0.3889	0.6111	2.24858×10^{-6}	8.85	7.00	2.09190×10^{-6}	-13.0774
	333	219911.5	1.20	1.50	35	0.3389	0.6111	3.15625×10^{-6}	8.85	7.00	2.93633×10^{-6}	-12.7384
	353	113097.3	1.50	1.40	32.5	0.3611	0.6389	9.85023×10^{-6}	9.09	6.82	9.03028×10^{-6}	-11.6149
	373	50265.5	1.30	1.50	31	0.3444	0.6556	1.59929×10^{-5}	9.00	6.68	1.46187×10^{-5}	-11.1332
	393	31415.9	1.35	1.55	29	0.3222	0.6778	2.59614×10^{-5}	9.05	6.73	2.37430×10^{-5}	-10.6482
	413	12566.4	1.35	1.65	28	0.3111	0.6889	5.94678×10^{-5}	9.14	6.73	5.42410×10^{-5}	-9.82207
	433	25132.7	0.90	1.20	47.5	0.5278	0.4722	2.16363×10^{-5}	7.93	6.57	2.03995×10^{-5}	-10.8000
	453	21991.1	1.10	0.90	47	0.5222	0.4778	6.92085×10^{-5}	7.86	6.50	6.52168×10^{-5}	-9.63779
	473	18849.6	1.00	1.10	45	0.5000	0.5000	4.38443×10^{-5}	7.86	6.50	4.13156×10^{-5}	-10.0943
	493	21991.1	1.40	0.90	42.5	0.4722	0.5278	1.05000×10^{-4}	8.41	6.41	9.67067×10^{-5}	-9.24383
	513	21991.1	1.80	0.95	32.5	0.3611	0.6389	1.24000×10^{-4}	8.68	6.45	1.13000×10^{-4}	-9.08762

Continued:

Compound	Temperature (K)	ω	v	u	$\alpha\,\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
HEAD	313	27646015.4	2.20	0.90	37.5	0.4167	0.5833	1.67425×10^{-7}	8.44	2.11	1.25568×10^{-7}	-15.8904
	333		2.10	1.05	37.5	0.4167	0.5388	1.18691×10^{-7}	8.44	2.00	8.85028×10^{-8}	-16.2402
	353		2.10	1.00	35.5	0.3944	0.6056	1.23161×10^{-7}	8.33	2.00	9.19641×10^{-8}	-16.2019
	373		2.05	1.00	39.5	0.4389	0.5611	1.30007×10^{-7}	8.33	2.00	9.70764×10^{-8}	-16.1478
	393		2.10	1.00	39	0.4333	0.5667	1.33965×10^{-7}	8.33	1.89	9.94414×10^{-8}	-16.1237
	413		2.10	1.05	37.5	0.4167	0.5833	1.18691×10^{-7}	8.11	1.78	8.78111×10^{-8}	-16.2481
	433		2.10	1.00	40	0.4444	0.5556	1.37519×10^{-7}	8.22	2.00	1.02832×10^{-7}	-16.0902
	453		2.05	1.10	37.5	0.4167	0.5833	1.05158×10^{-7}	8.11	1.78	7.77990×10^{-8}	-16.3691
	473		2.10	1.00	37.5	0.4167	0.5833	1.29046×10^{-7}	8.11	1.89	9.60549×10^{-8}	-16.1583

τ Ranges for AD and HEAD are (2.09190×10^{-6}-$1.13000\times10^{-4}$and 7.77990×10^{-8}- 1.25568×10^{-7}) respectively.

Compound	Temperature (K)	ω	v	u	$\alpha\,\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
TBA	313	21362830.0	1.00	2.50	31	0.3444	0.6556	1.15695×10^{-8}	11.39	2.78	8.65426×10^{-9}	-18.5652
	333		1.00	2.45	31	0.3444	0.6556	1.19316×10^{-8}	11.25	2.64	8.88770×10^{-9}	-18.5386
	353		1.00	2.45	32	0.3556	0.6444	1.16537×10^{-8}	11.11	2.36	8.59428×10^{-9}	-18.5722
	373		1.00	2.45	30	0.3333	0.6667	1.22065×10^{-8}	10.71	2.14	8.95069×10^{-9}	-18.5315
	393		1.00	2.40	31	0.3444	0.6556	1.23128×10^{-8}	10.71	2.14	9.02864×10^{-9}	-18.5229
	413		1.00	2.40	31	0.3444	0.6556	1.23128×10^{-8}	10.86	2.14	9.01732×10^{-9}	-18.5241
	433		1.00	2.40	33	0.3667	0.6333	1.17492×10^{-8}	10.11	3.44	9.16537×10^{-9}	-18.5078
	473		0.80	2.20	38	0.4222	0.5778	8.12751×10^{-9}	7.73	2.64	6.34360×10^{-9}	-18.8758
NBA	313	20106193.0	1.15	2.60	25	0.2778	0.7222	1.60744×10^{-8}	15.74	3.70	1.19758×10^{-8}	-18.2404
	333	22619467.1	1.30	2.10	27.5	0.3056	0.6944	2.21616×10^{-8}	12.14	3.82	1.70988×10^{-8}	-17.8843
	353	942477.8	1.70	1.00	32	0.3556	0.6444	2.41725×10^{-8}	22.50	9.44	1.94956×10^{-6}	-13.1479
	373	25132741.2	1.90	1.55	8.5	0.0944	0.9056	4.98200×10^{-8}	8.38	4.31	4.17545×10^{-8}	-16.9915
	393	20106193.0	0.90	2.35	30	0.3333	0.6667	1.17878×10^{-8}	11.03	2.79	8.85241×10^{-9}	-18.5426
	413	25132741.2	1.70	1.65	9	0.1000	0.9000	4.11307×10^{-8}	8.77	4.77	3.48774×10^{-8}	-17.1714
	433	21362830.0	1.00	2.40	31.5	0.3500	0.6500	1.21731×10^{-8}	10.00	4.29	9.85615×10^{-9}	-18.4352
	443	25132741.2	1.95	1.95	0	0.0000	1.0000	3.97887×10^{-8}	7.87	4.33	3.38230×10^{-8}	-17.2021
B	313	20106193.0	1.00	2.95	18	0.2000	0.8000	1.28645×10^{-8}	17.04	4.44	9.69367×10^{-9}	-18.4518
	333		1.20	2.75	20	0.2222	0.7778	1.61172×10^{-8}	16.11	3.70	1.19787×10^{-8}	-18.2401
	353		1.20	2.75	18.5	0.2056	0.7944	1.64818×10^{-8}	16.11	3.52	1.21883×10^{-8}	-18.2228
	373	21362830.0	1.20	2.75	20	0.2222	0.7778	1.61172×10^{-8}	16.11	3.52	1.19187×10^{-8}	-18.2452
	393		1.20	2.75	20	0.2222	0.7778	1.61172×10^{-8}	16.11	3.33	1.18553×10^{-8}	-18.2505
	413		1.20	2.75	20	0.2222	0.7778	1.61172×10^{-8}	16.11	3.33	1.18553×10^{-8}	-18.2505
	433	22619467.1	1.40	2.55	20	0.2222	0.7778	2.04504×10^{-8}	15.93	3.33	1.50586×10^{-8}	-18.0113

τ Ranges for TBA, NBA and B are (6.34360×10^{-9}- 9.16537×10^{-9}, 8.85241×10^{-9}- 1.94956×10^{-6} and 9.69367×10^{-9}- 1.50586×10^{-8}) respectively.

Compound	Temperature (K)	ω	v	u	$\alpha\,\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
PB	313	27646015.4	2.60	1.60	8	0.0889	0.9111	6.16300×10^{-8}	10.35	2.71	4.64656×10^{-8}	-16.8846
	333		2.60	1.60	8	0.0889	0.9111	6.16300×10^{-8}	10.12	2.47	4.61007×10^{-8}	-16.8924
	353		2.50	1.50	10	0.1111	0.8889	6.42610×10^{-8}	9.76	2.35	4.79982×10^{-8}	-16.8521
	373		2.40	1.50	10	0.1111	0.8889	6.13765×10^{-8}	9.53	2.12	4.54689×10^{-8}	-16.9062

Continued:

Compound	Temperature (K)	ω	v	u	$\alpha\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
	393		2.20	1.40	8.5	0.0944	0.9056	5.95847×10^{-8}	9.06	2.24	4.46337×10^{-8}	-16.9248
	413		2.20	1.40	8	0.0889	0.9111	5.94036×10^{-8}	8.82	2.00	4.40925×10^{-8}	-16.937
	423		2.10	1.40	13.5	0.1500	0.8500	5.82819×10^{-8}	8.35	1.76	4.29495×10^{-8}	-16.9632
TU	313	25132741.2	1.85	1.40	25	0.2778	0.7222	5.85274×10^{-8}	14.14	3.96	4.44819×10^{-8}	-16.9282
	333	25132741.2	2.00	1.40	32	0.3556	0.6444	6.92031×10^{-8}	13.29	4.57	5.40676×10^{-8}	-16.733
	353	25132741.2	1.95	1.40	32.5	0.3611	0.6389	6.68352×10^{-8}	12.86	4.43	5.22312×10^{-8}	-16.7676
	373	28902652.4	2.10	1.05	30	0.3333	0.6667	9.78605×10^{-8}	12.93	2.56	7.16988×10^{-8}	-16.4508
	393	28902652.4	2.10	1.05	29	0.3222	0.6778	9.62066×10^{-8}	12.93	2.37	7.00158×10^{-8}	-16.4745
	413	27646015.4	1.90	1.15	30	0.3333	0.6667	7.68159×10^{-8}	12.56	2.56	5.64295×10^{-8}	-16.6903
	433	26389378.3	1.90	1.25	33	0.3667	0.6333	7.33994×10^{-8}	12.31	3.38	5.56507×10^{-8}	-16.7042
	453	26389378.3	1.90	1.25	30	0.3333	0.6667	7.10127×10^{-8}	12.31	3.54	5.41489×10^{-8}	-16.7315
	473	27646015.4	2.20	1.05	31	0.3444	0.6556	1.11785×10^{-7}	11.86	3.43	8.52999×10^{-8}	-16.2771
	493	26389378.3	2.10	1.20	32.5	0.3611	0.6389	9.09868×10^{-8}	12.29	3.57	6.94678×10^{-8}	-16.4824
	513	26389378.3	2.00	1.30	32.5	0.3611	0.6389	7.43707×10^{-8}	12.31	3.08	5.57831×10^{-8}	-16.7018

τ Ranges for PB and TU are (4.29495×10^{-8}- 4.79982×10^{-8} and 4.44819×10^{-8}- 8.52999×10^{-8}) respectively.

Compound	Temperature (K)	ω	v	u	$\alpha\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
Hg(BA)$_2$	313	942477.8	1.60	1.00	32.5	0.3611	0.6389	2.21422×10^{-6}	7.89	5.42	1.98316×10^{-6}	-13.1308
	333	125663.7	1.05	1.30	26	0.2889	0.7111	5.89325×10^{-6}	7.75	5.25	5.25957×10^{-6}	-12.1555
	353	22619467.1	1.50	2.30	24	0.2667	0.7333	2.46818×10^{-8}	6.66	1.08	1.77887×10^{-8}	-17.8447
	373		1.50	2.35	24	0.2667	0.7333	2.39685×10^{-8}	6.38	1.38	1.77071×10^{-8}	-17.8493
	393		1.50	2.30	27	0.3000	0.7000	2.40062×10^{-8}	6.31	1.38	1.77542×10^{-8}	-17.8466
	413		1.40	2.10	27	0.3000	0.7000	2.47719×10^{-8}	6.17	0.96	1.77993×10^{-8}	-17.8441
	433		1.40	2.25	28	0.3111	0.6889	2.22027×10^{-8}	5.92	1.00	1.60520×10^{-8}	-17.9474
	453		1.35	2.05	23	0.2556	0.7444	2.52243×10^{-8}	6.00	0.96	1.81615×10^{-8}	-17.824
	473		1.30	2.05	24	0.2667	0.7333	2.37561×10^{-8}	6.00	0.87	1.69856×10^{-8}	-17.8909
	493	21362830.0	1.20	2.45	27.5	0.3056	0.6944	1.6748×10^{-8}	6.00	1.15	1.22353×10^{-8}	-18.2189
	513	21362830.0	1.25	2.40	27.5	0.3056	0.6944	1.82973×10^{-8}	6.15	1.31	1.34974×10^{-8}	-18.1208
Cr(TU)(OH$^-$)$_2$.H$_2$O	313	25132741.2	1.50	1.30	43.5	0.4833	0.5167	5.24864×10^{-8}	7.43	5.66	4.83185×10^{-8}	-16.8455
	333	20106193.0	0.95	2.10	37	0.4111	0.5889	1.29324×10^{-8}	6.53	2.93	1.05558×10^{-8}	-18.3666
	353	22619467.1	1.55	1.70	35	0.3889	0.6111	3.80077×10^{-8}	6.33	2.53	3.04021×10^{-8}	-17.3088
	373	25132741.2	1.75	1.60	32.5	0.3611	0.6389	4.578×10^{-8}	6.36	0.91	3.27034×10^{-8}	-17.2358
	393	25132741.2	1.75	1.60	33	0.3667	0.6333	4.58363×10^{-8}	6.36	0.91	3.27437×10^{-8}	-17.2346
	413	25132741.2	1.75	1.60	35	0.3889	0.6111	4.60728×10^{-8}	6.27	0.82	3.27237×10^{-8}	-17.2352
	433	25132741.2	1.70	1.50	35	0.3889	0.6111	4.88325×10^{-8}	6.00	1.00	3.52679×10^{-8}	-17.1603
	453	25132741.2	1.70	1.50	35	0.3889	0.6111	4.88325×10^{-8}	6.09	0.91	3.49873×10^{-8}	-17.1683
	473	25132741.2	1.70	1.50	35	0.3889	0.6111	4.88325×10^{-8}	6.09	1.00	3.52278×10^{-8}	-17.1614
	493	25132741.2	1.70	1.50	36	0.4000	0.6000	4.90181×10^{-8}	6.00	0.91	3.51569×10^{-8}	-17.1634
	513	25132741.2	1.70	1.50	36	0.4000	0.6000	4.90181×10^{-8}	6.00	0.82	3.49118×10^{-8}	-17.1704

τ Ranges for Hg(BA)$_2$ and Cr-(TU)(OH-)$_2$.H$_2$O are (1.22353×10^{-8}- 5.25957×10^{-6} and 1.05558×10^{-8} - 4.83185×10^{-8}) respectively .

Continued:

Com-pound	Tem-perature (K)	ω	v	u	$\alpha\,\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
Mn$(TU)_2\cdot$H$_2$O	313	25132741.2	1.90	1.85	25	0.2778	0.7222	4.12854×10^{-8}	8.56	1.33	2.96618×10^{-8}	-17.3334
	333	25132741.2	1.90	1.85	26	0.2889	0.7111	4.13092×10^{-8}	8.22	1.11	2.93989×10^{-8}	-17.3423
	353	25132741.2	1.75	1.65	23	0.2556	0.7444	4.30612×10^{-8}	7.89	1.56	3.15455×10^{-8}	-17.2718
	373	22619467.1	1.30	2.00	20	0.2222	0.7778	2.54084×10^{-8}	7.88	1.41	1.84544×10^{-8}	-17.808
	393	25132741.2	1.65	1.60	20	0.2222	0.7778	4.13945×10^{-8}	7.76	1.53	3.03168×10^{-8}	-17.3116
	413	23876104.2	1.40	1.70	22.5	0.2500	0.7500	3.23302×10^{-8}	7.41	1.41	2.36041×10^{-8}	-17.5618
	433	25132741.2	1.60	1.55	25	0.2778	0.7222	4.15769×10^{-8}	7.44	1.44	3.04003×10^{-8}	-17.3088
	453	25132741.2	1.60	1.55	24	0.2667	0.7333	4.15492×10^{-8}	7.33	1.44	3.04203×10^{-8}	-17.3082
	473	25132741.2	1.85	1.75	28	0.3111	0.6889	4.31313×10^{-8}	8.11	1.11	3.07220×10^{-8}	-17.2983
	493	25132741.2	2.00	1.80	28	0.3111	0.6889	4.63642×10^{-8}	8.56	1.33	3.33107×10^{-8}	-17.2174
	513	21362830.0	1.35	2.10	30	0.3333	0.6667	2.41275×10^{-8}	9.73	1.47	1.73001×10^{-8}	-17.8726
Co-Ni $(TU)_3\cdot$4 H$_2$O	313	26389378.3	2.30	1.70	20	0.2222	0.7778	5.58931×10^{-8}	9.00	1.56	4.04914×10^{-8}	-17.0222
	333		2.20	1.55	25	0.2778	0.7222	6.15401×10^{-8}	8.56	1.44	4.44776×10^{-8}	-16.9283
	353		2.00	1.45	25	0.2778	0.7222	5.91492×10^{-8}	7.89	1.33	4.27564×10^{-8}	-16.9677
	373		1.70	1.40	20	0.2222	0.7778	$4.86389\times1^{0-8}$	7.29	1.29	3.52949×10^{-8}	-17.1595
	393		2.00	1.45	30.5	0.3389	0.6611	6.16346×10^{-8}	6.91	1.36	4.51333×10^{-8}	-16.9136
	413		1.95	1.50	30	0.3333	0.6667	5.61676×10^{-8}	6.91	1.18	4.06423×10^{-8}	-17.0185
	433		2.10	1.30	31	0.3444	0.6556	7.87553×10^{-8}	6.54	1.85	5.99295×10^{-8}	-16.6301
	453		1.95	1.40	30	0.3333	0.6667	6.22918×10^{-8}	6.73	1.36	4.57238×10^{-8}	-16.9006
	473		2.15	1.25	31	0.3444	0.6556	8.66666×10^{-8}	6.62	1.85	6.58509×10^{-8}	-16.5359
	493		2.00	1.45	31	0.3444	0.6556	6.18892×10^{-8}	6.73	1.27	4.51524×10^{-8}	-16.9132
	513	21362830.0	1.10	2.00	20	0.2222	0.7778	2.17031×10^{-8}	7.22	1.22	1.56912×10^{-8}	-17.9702

τ Ranges for Mn(TU)$_2$.H$_2$O and Co-Ni(TU)$_3$.4H$_2$Oare (1.73001×10^{-8} - 3.33107×10^{-8} and 1.56912×10^{-8} - 6.58509×10^{-8}) respectively.

Com-pound	Tem-perature (K)	ω	v	u	$\alpha\,\pi/2$	α	$1-\alpha$	τ_o	ε_s	ε_∞	τ	$\ln\tau$
Hg $(TU)_2$.4 H$_2$O	313	21362830.0	1.70	2.50	16	0.1778	0.8222	2.92844×10^{-8}	9.33	1.67	2.12701×10^{-8}	-17.666
	333		1.20	2.10	17	0.1889	0.8111	2.34804×10^{-8}	7.89	1.89	1.75285×10^{-8}	-17.8594
	353		1.05	1.90	15	0.1667	0.8333	2.29755×10^{-8}	7.73	1.60	1.69022×10^{-8}	-17.8958
	373		1.10	2.10	20	0.2222	0.7778	2.03835×10^{-8}	7.53	1.41	1.48613×10^{-8}	-18.0245
	393		1.10	2.10	22.5	0.2500	0.7500	1.97654×10^{-8}	7.29	1.18	1.42434×10^{-8}	-18.067
	413		1.30	2.20	30	0.3333	0.6667	2.12629×10^{-8}	7.18	1.45	1.56066×10^{-8}	-17.9756
	433		1.10	2.40	30	0.3333	0.6667	1.45249×10^{-8}	7.18	1.64	1.07892×10^{-8}	-18.3447
	453		1.10	2.10	21	0.2333	0.7667	2.01394×10^{-8}	7.44	1.44	1.47256×10^{-8}	-18.0337
	473		1.10	1.80	0	0.0000	1.0000	2.86063×10^{-8}	7.47	1.73	2.12792×10^{-8}	-17.6655
	493	942477.8	2.10	1.90	14	0.1556	0.8444	1.19454×10^{-6}	21.14	7.05	9.29151×10^{-7}	-13.889
	513	4398.2	1.20	1.50	25	0.2778	0.7222	1.67000×10^{-4}	24.55	14.09	1.43000×10^{-4}	-8.8511

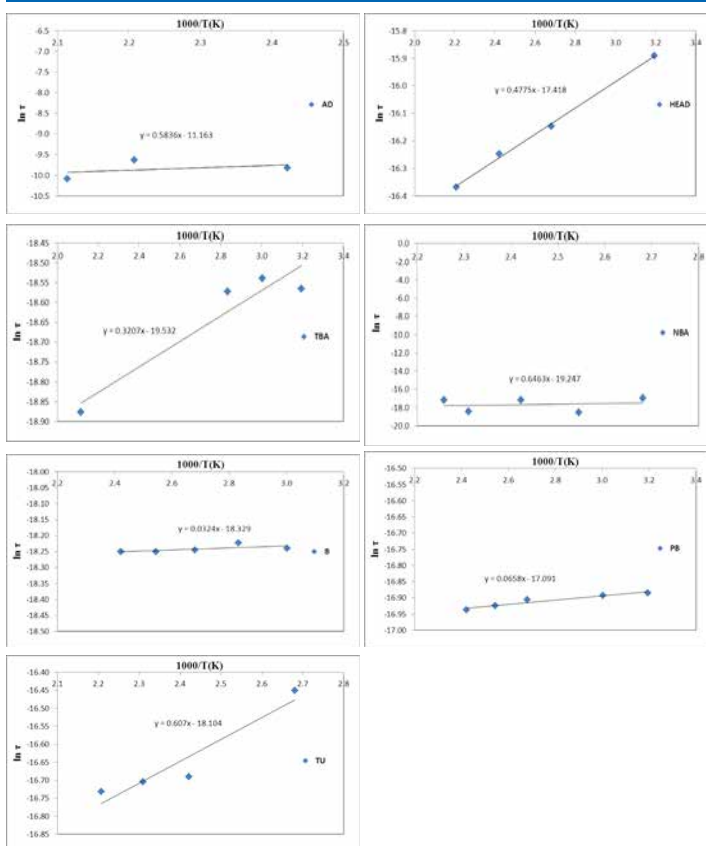τ Ranges for Hg(TU)$_2$.4H$_2$Ois (1.07892×10^{-8}- 1.43000×10^{-4}).
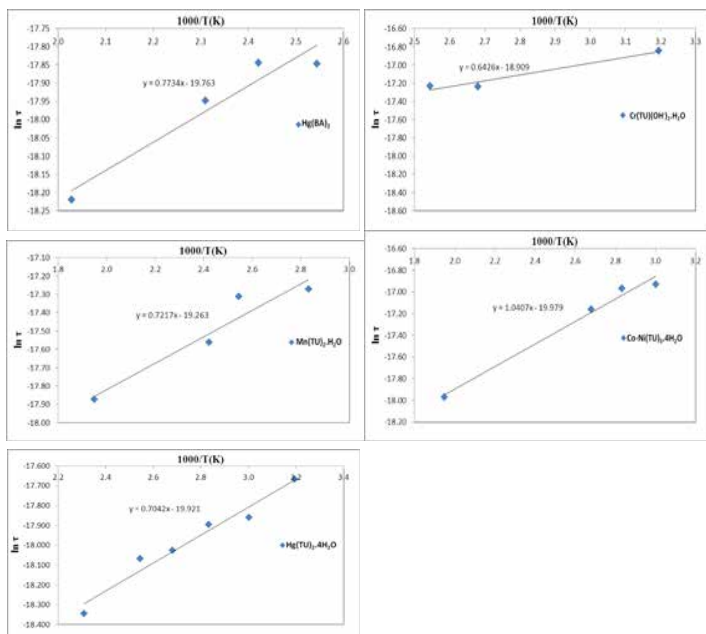
Figure 28: ln τ-1000/T relationship for ligands

Figure 29: ln τ-1000/T relationship for complexes

Table 4: The activation energies E_o(kJ mol^{-1}) for the relaxation processes of compounds

Compound	E_o(kJ mol^{-1})
AD	4.85
HEAD	3.97
TBA	2.66
NBA	5.37
B	0.27
PB	0.54
TU	5.05
$Hg(BA)_2$	6.43
$Cr(TU)(OH^-)_2.H_2O$	5.34
$Mn(TU)_2.H_2O$	5.99
$Co\text{-}Ni(TU)_3.4H_2O$	8.65
$Hg(TU)_2.4H_2O$	5.85

Electrical Conductivity Measurements

The alternating current conductivity(σ) is calculated according to the following equation [10]:

$$\sigma\ (\Omega^{-1}\ cm^{-1}) = \omega \times C_P\ (pF) \times \tan \delta \times \frac{d}{A}\ (cm^{-1}) \times 10^{-12}$$

The frequency dependence of a. c. conductivity for ligands and complexes at different temperatures is illustrated in Figures (30, 31). The behavior shows that the a. c. conductivity gradually increases with increasing the frequency. At lower frequencies the grain boundaries are more effective than grains in electrical conduction hence the hopping of ions are bound at lower frequencies. As the frequency of the applied field increases the conductive grains become more active and promote the conduction mechanism [25].

From the practical standpoint, materials may be classified according to their conductivities into three categories [14]:

Conductivity range

i.   Conductors 10^6-$10^8 \Omega^{-1}\ m^{-1}$
ii. Semiconductors 10^5-$10^{-7} \Omega^{-1}\ m^{-1}$
iii. Insulators 10^{-8}-$10^{-20} \Omega^{-1}\ m^{-1}$

However, the conductivity of the conductors decreases with increasing temperature whilst that of semiconductors and insulators increases with increasing temperature [14].

In the present ligands and complexes, the conductivities have a magnitude close to that of semiconductors, where the electrons in

the orbitals are not of sufficient mobility to be promoted [26-33]. The study of the conduction mechanism of organic materials leads to an increasing use of these materials in commercial devices such as solar energy panels, scintillation counter and also in some technological applications such as photocopy process [34].

The investigation of electron transport in disorder systems has been gradually developed.

The investigation of gap states is of particular interest, because of their effect on the electrical properties of semiconductor materials [35, 36]. Several concepts proposed by many workers start from the premise that the contribution of carriers hopping between localized states to electrical conductivity is expected in amorphous semiconductors [37-39]. The hopping conduction can be easily distinguished from that of the band conduction by measuring the frequency dependence of conductivity, which as expected, is due to conduction in localized states [39-42].

Theories proposed for a.c. conduction in amorphous semiconductors have mostly assumed that carrier motion occurs through quantum mechanical tunneling (QMT) between localized states near the Fermi-level [43, 44].

The classification of organic compounds on the basis of semiconducting properties was originally proposed by Garrett [45]. This classification consisted of polymers, charge transfer (CT) complexes and molecular crystals. Another mode of classification was given to four groups [46]: (i) molecular crystals bonded by relatively weak Van der Waals forces, (ii) complexes which also exhibit, in addition to the Van der Waals interaction, a varying degree of covalent and coordinate bonding, (iii) polymers which are really macromolecules held together by ionic and covalent bonding, and (iv) free radicals or their salts.

Eley proposed a theory of charge carrier formation and migration in organic semiconductor based on simplified assumption that the electron should tunnel from the first excited molecular orbital through a conductivity of levels [47-49]. Hansel model for electrical conduction mechanism of organic solids is based on [50]:
1. The conductivity depends on the mobility of π-electrons.
2. In the molecule, the π-electrons are localized in the molecule framework and their delocalization requires activation energy.
3. The delocalized π-electrons migrate to the neighbouring molecule by tunnel effect. As the temperature increases, the bonds are exhausted resulting in an increase of the conductivity.
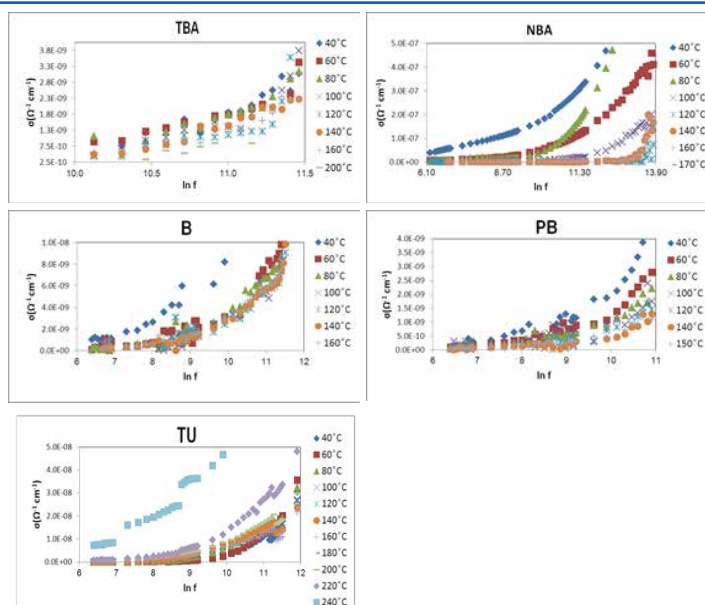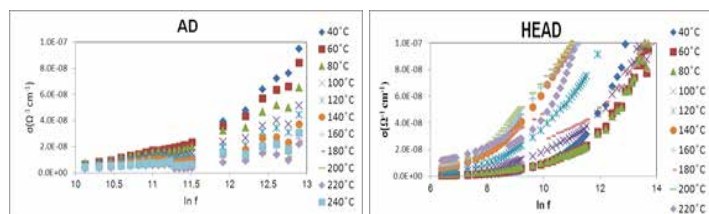
Figure 30: A.C. conductivity σ-lnf relationship for ligands at different temperatures

Figure 31: A.C. conductivity σ-lnf relationship for complexes at different temperatures ◆40°C,■60°C,▲80°C,✕100°C,✕120°C,●140°C, ┼160°C,■180°C,⁻200°C,●220°C and ■240°C

The electrical conductivity of substances at a given frequency varies exponentially with the absolute temperature according to the Arrhenius relation [51]:

$$\sigma = \sigma_o\, e^{-\Delta E/kT}$$

where σ is the electrical conductivity at an absolute temperature T, σ_o is the pre-exponential factor, ΔE is the activation energy.

Therefore, the temperature dependence of the electrical conductivity is characterized by the two constants: the activation energy (ΔE) and the pre-exponential factor (σ_o).

The variations of ln σ as a function of reciprocal absolute temperature for ligands and complexes at different frequencies are illustrated in Figures (32, 33). The activation energy data and ln σ_o values for ligands and complexes are given in Table (5).

A discontinuity in the conductivity curve at a transition temperature can be ascribed to a molecular rearrangement or different crystallographic or phase transitions [52, 53]. The magnitude of the conductivities along with the values of the energy gaps indicated slight semiconducting properties. The most realistic description of the complexes involves an interaction of the metal orbitals with the ligands to give new molecular orbitals (MO), which are delocalized over the whole molecular complex. In view of the high degree of covalency in the M-O and M-N bonds, it is no longer permissible to distinguish the central metal from the ligands. The complexes must be regarded as individual entities.

The experimental results of a.c. conductivity σ, have been analyzed in terms of various theoretical models. Application of correlated barrier-hopping (CBH) model reveals that electronic conduction takes place by bipolaron or mixed polaron hopping process [54].

The relationship between molecular structure and electrical properties was deduced [55, 56]. On the basis of electronic transition within molecules, two pathways for the conduction of electricity may be expected [57]. The first conducting process occurring in the lower temperature region is attributed to n→π* transitions which require less energy to be performed. In the upper temperature region, conduction could be attributed to π→π* transitions which need more energy to participate in electronic conduction. The observed increment of conduction in the upper temperature region may be attributed to interactions between n→π* and π→π* transitions.

The lower temperature range is the region of extrinsic semiconductor where the conduction is due to the excitation of carriers from donor localized level to the conduction band. In the upper temperature range, the intrinsic region is reached where carriers are thermally activated from the valence band to the conduction band [58]. This behavior can be explained as follows: the upper temperature range may be attributed to the interaction between the electrons of d-orbitals and the p-orbitals of the ligand [59]. This interaction will lead to small delocalization of the p-electronic charge on the ligand which tends to increase the activation energy. The presence of d-electrons in a narrow energy band leads to magnetic ordering and degeneracy of d-bands with respect to the orbital quantum number, which is only partially lifted in a crystal field [60, 61].

In all ligands and complexes, during thermal agitation, an additional increase in electrical conductivity occurs, which probably indicating a discontinuity of the chemical bonds existing in the

structure. This is a useful criterion for ascertaining the nature of the metal-ligand bonding [62].

It is found that the activation energy decreased with increasing the atomic number of the metal in the $Mn(TU)_2.H_2O$ and $Hg(TU)_2.4H_2O$ complexes , which indicates that the presence of holes in the system has little effect on the mobility of charges [63, 64].

For the complexes, the metal ion forms a bridge with the ligands, thus facilitating the transfer of current carriers with some degree of delocalization in the excited state during measurements. Meanwhile, this leads to an increase of the electrical conductivity with a decrease in energy of activation [65].
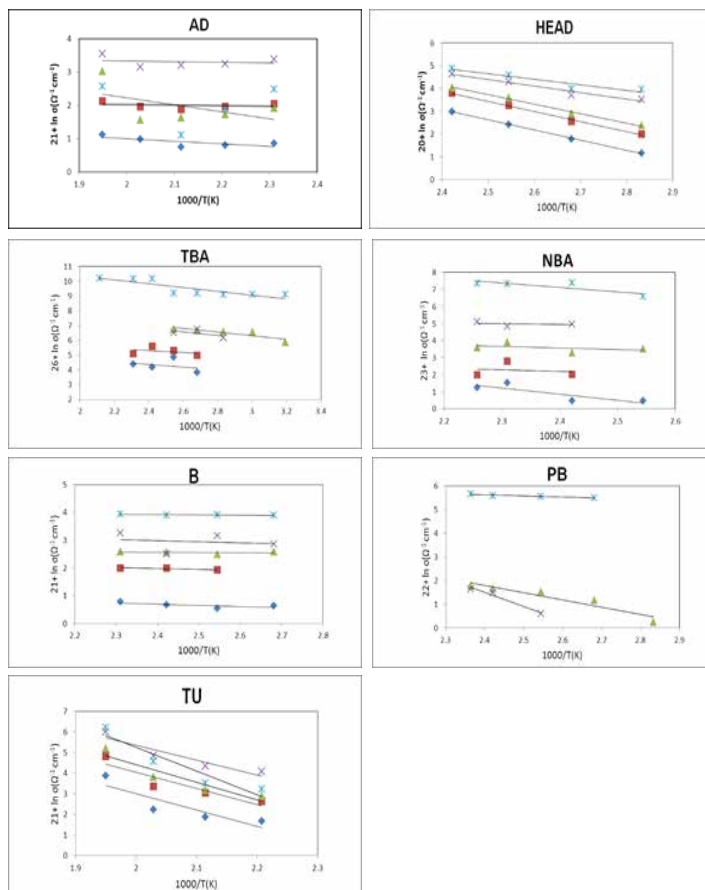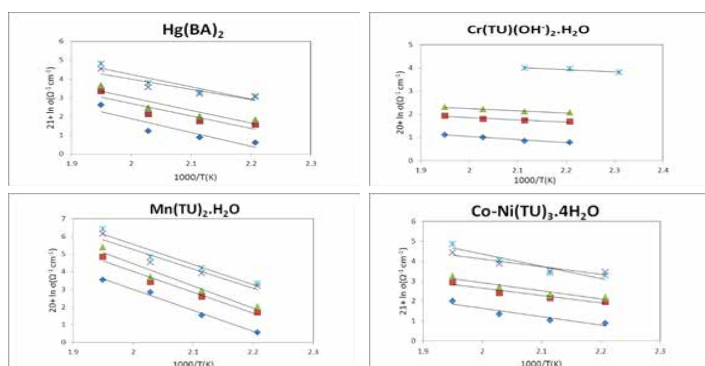

Figure 32: ln σ-1000/T relationship for ligands at different frequencies ◆10 kHz, ■50 kHz, ▲100 kHz ×500 kHz and ✕1000 kHz
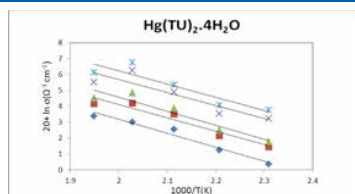
Figure 33: ln σ-1000/T relationship for complexes at different frequencies ●10 kHz,■50 kHz,▲100 kHz, ⨯500 kHz and ⨯1000 kHz

Table 5: The activation energy data ΔE(kJ mol⁻¹) and ln σₒ values for compounds at different frequencies

Compound	Frequency(kHz)	$\ln \sigma_o$	$\Delta E(kJ\ mol^{-1})$
AD	10	-18.50	6.24
	50	-18.66	1.33
	100	-14.57	17.43
	500	-17.27	1.67
	1000	-18.67	1.20
HEAD	10	-6.23	37.09
	50	-5.51	36.78
	100	-5.87	34.61
	500	-8.46	23.79
	1000	-9.28	20.22
TBA	10	-19.53	7.23
	50	-19.19	5.22
	100	-15.95	10.36
	500	-16.32	9.89
	1000	-13.09	10.63
NBA	10	-13.55	29.70
	50	-18.43	8.23
	100	-17.29	7.45
	500	-16.93	3.92
	1000	-9.69	21.43
B	10	-19.22	3.76
	50	-18.31	2.49
	100	-18.28	0.56
	500	-17.12	3.14
	1000	-16.90	0.62
PB	100	-12.90	25.36
	500	-6.10	49.88
	1000	-15.17	4.16
TU	10	-2.18	65.78
	50	-1.23	65.38
	100	0.55	71.27
	500	-1.21	60.04
	1000	7.25	95.70

Continued:

Compound	Frequency(kHz)	ln σ_o	ΔE(kJ mol^{-1})
Hg(BA)$_2$	10	-4.47	60.91
	50	-5.13	54.84
	100	-4.44	56.39
	500	-6.06	45.55
	1000	-3.71	54.32
Cr(TU)(OH$^-$)$_2$.H$_2$O	10	-16.33	10.97
	50	-16.21	8.02
	100	-15.84	7.96
	1000	-15.78	8.18
Mn(TU)$_2$.H$_2$O	10	6.88	99.23
	50	7.70	98.40
	100	9.66	104.81
	500	7.26	91.40
	1000	8.36	94.82
Co-Ni(TU)$_3$.4H$_2$O	10	-11.01	34.78
	50	-10.96	30.76
	100	-10.02	33.58
	500	-9.23	31.86
	1000	-4.39	50.94
Hg(TU)$_2$.4H$_2$O	10	0.76	73.11
	50	0.87	69.70
	100	2.20	73.30
	500	2.03	67.99
	1000	2.84	69.11

Molecular Modeling

The molecular modeling calculations are widely increasing nowadays for the expectation of the mechanism of the reactions and the identification of the products [66].

This saves time and money. The multidentate ligands including nitrogen, sulphur and oxygen atoms are versatile and useful for assembly new molecules, because they can coordinate many transition metal ions. Thus, the syntheses and structures of new complexes are significant for understanding the biological phenomena and exploiting artificial models [67].

Also, a theoretical support for the experimental findings regarding the donor atoms could be obtained on comparing the molecular models of the complexes with that of the free ligands.

For example the molecular modeling calculations of the compounds BA and Hg(BA)$_2$, Figures (34, 35) (a(ChemOffice modeling), b(HyperChem modeling)) are given concerning the bond lengths, bond angles, dihedral angles and HyberChem data. These calculations are based on using molecular orbital package (MO-PAC) for minimizing energies where the Austin Model 1(AM1) method is used, also Parameterized Model 3(PM3) is applied for HyberChem.

Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular orbital energy (E_{LUMO}) were given using HyberChem modeling, where energy gap (ΔE) and parameters which give information about the reactive chemical behavior of compounds such as electronegativity (χ), chemical potential (μ), global hardness (η), softness (σ) and electrophilicity index (ω) were calculated, Table (6).

$$\Delta E = E_{LUMO} - E_{HOMO}$$

The concepts of these parameters are related to each other, the energies of the (HOMO) and (LUMO) orbitals of the molecule are related to ionization potential (I) and the electron affinity (A), respectively, and their relations with χ and μ are given by the following equations [68-72]:

$$I = -E_{HOMO} \qquad \mu = -\chi$$

$$A = -E_{LUMO} \qquad \mu = \frac{-(I+A)}{2} = \frac{E_{HOMO} + E_{LUMO}}{2}$$

Large χ values characterize acids and small χ values are found for bases.

The qualitative definition of hardness is related to the polarizability, because a decrease of the energy gap usually leads to an easier polarization of the molecule [68].

$$\eta = \frac{I-A}{2} = \frac{E_{LUMO} - E_{HOMO}}{2}$$

The inverse of the hardness is equal to softness, (σ) as follows:

$$\sigma = \frac{1}{\eta}$$

The energy difference between the HOMO and LUMO (HOMO-LUMO gap) can be used to predict the strength and stability of transition metal complexes.

Hard molecules have a large HOMO-LUMO gap while, soft molecules have a small HOMO-LUMO gap.

Soft molecules have small excitation energies to the excited states, therefore they will be more polarizable and more reactive than the hard molecules.

Hard molecules resist changes in their electron number and distribution.

The electrophilicity index (ω) in terms of chemical potential (μ) and hardness (η) is given from the equation [73-75]:

$$\omega = \frac{\mu^2}{2\eta}$$

BA, TBA and B have a largest values of χ, Table (6).

HOMO-LUMO gap is decreased and softness increased upon complexation with BA ligand, which give stabilization for complex formation.
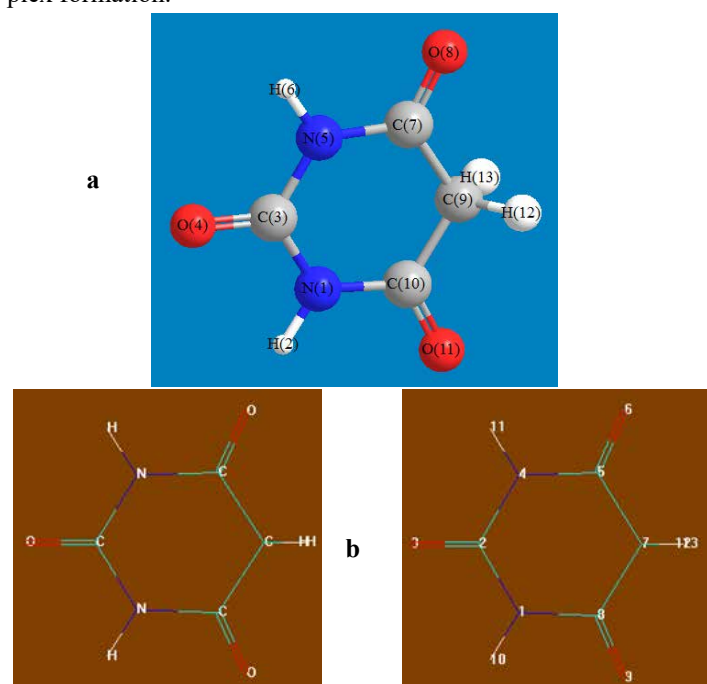

Figure 34: The molecular modeling of Barbituric acid (BA), a)

ChemOffice, b) HyperChem

HyperChem Calculations
Total energy: -40174.049 (kcal/mol).
Binding energy: -1420.823 (kcal/mol).
Isolated atomic energy: -38753.226 (kcal/mol).
Electronic energy: -165585.243 (kcal/mol).
Core-core interaction: 125411.193 (kcal/mol).
Heat of formation: -124.178(kcal/mol).
Dipole moment: 0.810 Debye.
HOMO: -10.828eV; **LUMO:** -0.421eV.
Net charges of atoms: (1(-0.024), 2 (0.230), 3(-0.361), 4(-0.024), 5(0.251), 6(-0.334), 7(-0.145), 8(0.251), 9(-0.334),10(0.127),11(0.127),12 (0.117) and 13(0.118)).
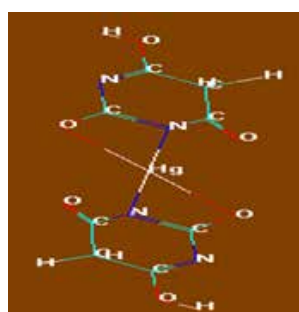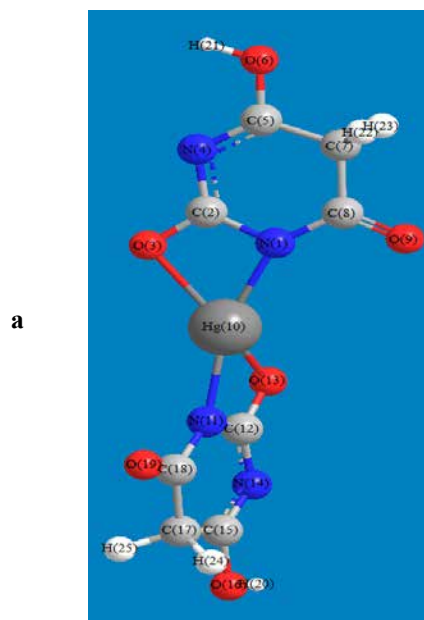
Figure 35: The molecular modeling of Hg(BA)$_2$, a) ChemOffice, b) HyperChem

HyperChem Calculations
Total energy: -80283.147 (kcal/mol).
Binding energy: -2713.185 (kcal/mol).
Isolated atomic energy: -77569.963 (kcal/mol).
Electronic energy: -447712.500 (kcal/mol).
Core-core interaction: 367429.353 (kcal/mol).
Heat of formation: -209.409 (kcal/mol).
Dipole moment: 3.087 Debye.
HOMO: -10.030eV; **LUMO:** -0.652eV.

Net charges of atoms: (1(-0.317), 2(0.328), 3(-0.343), 4(-0.251), 5(0.168), 6(-0.229),7(-0.097), 8(0.283), 9(-0.369),10(0.745),11(-0.317),12(0.327),13(-0.343),14(-0.251),15(0.168),16(-0.229),17(-0.097), 18(0.283), 19(-0.369), 20(0.237), 21(0.237), 22(0.111), 23(0.109), 24(0.111) and 25(0.109)).

Table 6: Quantum chemical parameters (eV) of compounds calculated by PM3 method

Compound	E_{HOMO}	E_{LUMO}	$\Delta E= (E_L-E_H)$	χ	μ	η	σ	ω
AD	-8.557	-0.234	8.323	4.3955	-4.3955	4.1615	0.2403	2.3213
HEAD	-8.778	-0.411	8.367	4.5945	-4.5945	4.1835	0.2390	2.5229
BA	-10.828	-0.421	10.407	5.6245	-5.6245	5.2035	0.1922	3.0398
Hg(BA)$_2$	-10.030	-0.652	9.378	5.3410	-5.3410	4.6890	0.2133	3.0418
TBA	-9.529	-1.750	7.779	5.6395	-5.6395	3.8895	0.2571	4.0884
B	-10.761	-0.328	10.433	5.5445	-5.5445	5.2165	0.1917	2.9466
PB	-8.388	-1.077	7.311	4.7325	-4.7325	3.6555	0.2736	3.0634
TU	-9.278	-1.343	7.935	5.3105	-5.3105	3.9675	0.2520	3.5541
Hg(TU)$_2$.4H$_2$O	-9.251	-1.265	7.986	5.2580	-5.2580	3.9930	0.2504	3.4619

References

1. GE Pike (1972) ac Conductivity of Scandium Oxide and a New Hopping Model for Conductivity. Phys Rev, B6, 1572, Philos B Mag 1972: 6.
2. SR Elliott (1977) A theory of a.c. conduction in chalcogenide glasses. Philos Mag 36: 1291-1304.
3. SS Kim and WJ Kim (2005) Electrical properties of sol–gel derived pyrochlore-type bismuth magnesium niobate $Bi_2(Mg_{1/3}Nb_{2/3})_2O_7$ thin films. J Crystal Growth 281: 432-439.
4. PS Anantha and K Hariharan (2005) ac Conductivity analysis and dielectric relaxation behaviour of $NaNO_3–Al_2O_3$ composites. J Materials Science and Engineering B 121: 12-19.
5. HM Zaki (2005) AC conductivity and frequency dependence of the dielectric properties for copper doped magnetite. J Physica B: Condensed Matter 363: 232-244.
6. M Okutan, E Basaran, HI Bakan and F Yakuphanoglu (2005) AC conductivity and dielectric properties of Co-doped TiO_2. J Physica B: Condensed Matter 364: 300-305.
7. AA Hendi (2011) AC Conductivity and Dielectric Measurements of Bulk Tertracyanoquinodimethane. Aust J Basic& Appl Sci 5: 380-386.
8. W Brütting (2004) Physics of Organic Semiconductors. Phys Stat Solidi A 201: 1035.
9. A Vogel (2004) Textbook of Quantitative Chemical Analysis. 4th Indian Reprint.
10. AK Jonscher (1983) Dielectric Relaxation in Solids. Chelsea Dielectric, London.
11. JS Blakemore (1995) Solid State Physics. 2nd Ed, Cambridge Univ Press.
12. HM Rosenberg (1997) The Solid State. 3rd Ed, Oxford Univ Press.
13. H Fröhlich (1949) Theory of Dielectrics. Oxford Univ Press, London.
14. AA Zaky and R Hawley (1970) Dielectric Solids. Routledge and Kegan Paul Ltd, London, UK.
15. A Vasudevan, S Carin, MR Melloch, ES Harmon (1998) Permittivity of GaAs epilayers containing arsenic precipitates. Appl Phys Lett 73: 671.
16. HM Lin, YF Chen, JL Shen and WC Chou (2001) Dielectric studies of $Cd_{1-x-y}Zn_xMn_y$Te crystals. J Appl Phys 89: 4476-4479.
17. B Tareev (1979) Physics of Dielectric Materials. Mir Publishers, Moscow.
18. S Kurien, J Mathew, S Sebastian, SNPotty and KC George (2006) Dielectric behavior and ac electrical conductivity of nanocrystalline nickel aluminate. Mater Chem Phys 98: 470-476.
19. JM Thomas (1977) Prospects in solid state chemistry. Chemistry in Britain 13: 175-182.
20. MM Ahmad, K Yamada and T Okuda (2002) Frequency dependent conductivity and dielectric studies on $RbSn_2F_5$. Solid State Communications 123: 185-189.
21. VV Daniel (1967) Dielectric Relaxation. Academic Press, London and New York.
22. KS Cole and RH Cole (1941) Dispersion and Absorption in Dielectrics I. Alternating Current Characteristics. J Chem Phys 9: 341.
23. MS Masoud, AE Ali, RH Mohamed and M Abd El-Zaher Mostafa (2005) Dielectric relaxation Spectroscopy of hetreonuclear cobalt(II) copper(II) complex of 1-phenyl-3-methyl-5-pyrazolone. Spectrochim Acta 62: 1114-1119.
24. E Şentürk (2004) Dielectric characteristics of Ce^{3+} doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ with Cole-Cole plots technique. Cryst Res Technol 39: 157-160.
25. K Verma, A Kumar and D Varshney (2012) Dielectric relaxation behavior of $A_xCo_{1-x}Fe_2O_4$ (A = Zn, Mg) mixed ferrites. J Alloys Compd 526: 91-97.
26. MS Masoud, ME Kassem, Y Abd El-Aziz and S Massoud (1987) Electrical conductivity of some azo complexes containing sulphur. Xth Conference on Solid State Science and Applications 1987: 46.
27. TM Salem, MM Osman, MS Masoud, MF El-Shazly, MM

Abou-Sekkina (1979) Electrical conductivity mechanisms in inorganic solids. Al Physica 2: 43.

28. MS Masoud, BS Farag, YA Sawan, TM Salem and MM El-Essawy (1983) Electrical conductivity of 2,4-dinitrosoresorcinol and its complexes. J Non-Crystalline Solids 55: 209-213.

29. A El-Dessouky, A El-Sonbati and M Kassem (1986) Metal chelates of heterocyclic nitrogen-containing ketones: XVII. effect of temperature and gamma irradiation on the electrical conductivity of 2-quinaldyl phenyl ketone and its metal complexes. Thermochim Acta 103: 213.

30. MS Masoud, ME Kassem, S Hedewy and AR Youssef (1987) Conducting properties of 3-amino-4-(substituted phenylazo)-5-(1H)-pyrazolone ligands and their complexes. 1st Regional Symposium of Materials Science (In the Arab States), Alex.

31. MS Masoud, EM Soliman and M El-Shabasy (1988) Effect of temperature on the electrical conductivity of some 4-(substituted)- 3-hydroxy-2-quinoline ligands and their complexes. Thermochim Acta 125: 9-16.

32. MS Masoud, A El-Khatib, M Kassem and AR Youssef (1988) Effect of Fast Neutron Irradiation on the Electrical conductivity of Some Azo Pyrazolones at Different Temperatures. J Mater Sci Lett 7: 1291-1294.

33. MS Masoud, GB Mohamed, ME Kassem, A El-Dessouky, AM Hindawy, et al. (1990) Temperature-electrical conductivity relations for 5-nitro- and 6-nitrobenzimidazole and their transition metal complexes. Thermochim Acta 159: 215-223.

34. AT Vartanyan (1947) Acta Phys Chem. USSR 22: 201.

35. W Beyer, H Mell, J Stuke (1971) Conductivity and Thermoelectric Power of Trigonal Se_xTe_{1-x} Single Crystals. J Phys Status Sol 45: 153-162.

36. AI Gubanov (1965) Quantum electron theory of amorphous conductors. consultants Bureau.

37. MH Cohen, H Fritzsche and SR Ovshinsky (1969) Simple Band Model for Amorphous Semiconducting Alloys. Phys Rev Lett 22: 1065.

38. EA Davis and NF Mott (1970) Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. Phil Mag 22: 903-922.

39. M Pollalk (1971) Proc Inter Conf Physics Semiconductors, Institute of Physics and physical society, London; Phil Mag 22: 519.

40. X Ledeac (1979) J Physique 40: 27.

41. K Shimakawa (1978) Phil Mag 46: 123.

42. M Pollak and GE Pike (1972) ac Conductivity of Glasses. Phys Rev Lett 28: 1449.

43. LG Austin and NF Mott (1969) Polarons in crystalline and non-crystalline materials. Adv Phys 18: 41-102.

44. CA Hogarth, MH Islam and ASMS Rahman (1993) D.c. and a.c. electrical properties of vacuum evaporated thin SiO/GeO_2 films. J Materials Science 28: 518-528.

45. CGB Garrett (1960) Mater Des Eng 51: 12.

46. F Gutmann and LE Lyons (1967) "Organic Semiconductors". Wiley, New York 1967: 5.

47. DD Eley (1948) Phthalocyanines as Semiconductors. Nature 162: 819.

48. DD Eley, GD Parfitt, MJ Perry and DH Taysum (1953) The semiconductivity of organic substances. Part 1. Trans Faraday Soc 49: 79.

49. DD Eley and GD Parfitt (1955) The semiconductivity of organic substances. Part 2. Trans Faraday Soc 51: 1529.

50. H Hansel (1970) Diffusion of metals in metals. Ann Phys 24: 1947.

51. DC Olson, VP Mayweg and GN Schrauzer (1966) Polarographic Study of Coordination Compounds with Delocalized Ground States. Substituent Effects in Bis- and Trisdithiodiketone Complexes of Transition Metals. J Am Chem Soc 88: 4874-482.

52. F Gutmann and A Netschey (1962) Electrical Properties of Chlorpromazine. J Chem Phys 36: 2355.

53. F Gutmann and H Keyzer (1965) Electrical Conduction in Chlorpromazine. Nature 205: 1102-1103.

54. MS Hossain, R Islam and KA Khan (2008) Electrical conduction mechanisms of undoped and Vanadium dopped ZnTe thin. Chalcogenide Letters 5: 1.

55. AH Pohl (1964) Physico-chemical aspects of organic semiconductors. Prog Solid State Chem 1: 316.

56. JJ Brophy and WJ Buttrey (1962) Organic Semiconductors. Proceeding of an Inter-Industry Conference, Macmillan.

57. SS Haggag, MM Syiam, HM Klash, II Mahmoud (2004) Hardware implementation of neural network on FPGA for accidents diagnosis of the multi-purpose research reactor of Egypt. IEEE 43: 77.

58. AA Shabana, KA El-Manakhly and HA Hammad (1994) Can J Appl Spectrosc 39: 151.

59. BA El-Sayed, MM El-Desoky, SM Shaaban and MB Sayed (1990) Electrical and spectral studies of solid organic semiconductors I. Structural interpretation of promoted conductivity of salicylaldazine. Electrochim Acta 35: 1987.

60. MS Masoud, ME Kassem, Y Abd El-Aziz and SM Khalil (1991) Electrical conductivty of some azo complexes containing sulphur. Bull Fac Sci, Mansoura University 18: 105-118.

61. MS Masoud, EA Khalil, EEl-Shereafy and SA Abou El-Enein (1990) Thermal and electrical behaviour of nickel (II) and copper (II) complexes of 4-acetamidophenylazo-p-cresol (4-acetylamino-2-hydroxy-5-methyl azobenzene) J Therm Anal 36: 1033-1036.

62. MS Masoud, ZM Zaki, FM Ismail and AK Mohamed (1997) Electrical conductivity behaviour of 5-substituted arylazothiobarbituric acid complexes at different temperatures. Z Phys Chem, Bd 185: 223-231.

63. MS Masoud, ZM Zaki and FM Ismail (1989) Conducting Properties of Some New Azo-Nitroso Complexes. Thermochim Acta 156: 225-230.

64. AAG Tomlinson and BJ Hathaway (1968) The Electronic Properties and Stereochemistry of the Copper(II) Ion. Part III. Some Penta-ammine Complexes. J Chem Soc A 1968: 1905-1909.

65. E El-Shereafy, SA Abou El-Enein, M Khider and H El-Esawy (2004) Bull Fac Sci Alex Univ 43: 67.

66. S Chen, JF Richardson and RM Buchanan (1994) Synthesis and Characterization of Copper(II) Complexes of New Tripodal Polyimidazole Ligands. Inorg Chem 33: 2376-2382.

67. Y Dong, H Fujii, MP Hendrish, RA Leising, G Pan, et al. (1995) A High-Valent Nonheme Iron Intermediate. Structure and Properties of $[Fe_2(\mu\text{-}O)_2(5\text{-}Me\text{-}TPA)_2](C1O_4)_3$. J Am Chem Soc 117: 2778-2792.

68. RG Pearson (1986) Absolute electronegativity and hardness correlated with molecular orbital theory. Proc Natl Acad Sci 83: 8440-8441.

69. T Koopmans (1934) Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms. Physica 1: 104-113.

70. RG Parr, RA Donnelly, M Levy and WE Palke (1978) Electronegativity: The density functional viewpoint. J Chem Phys 68: 3801.

71. RG Parr and RG Pearson (1983) Absolute hardness: companion parameter to absolute electronegativity. J Am Chem Soc 105: 7512-7516.

72. EM Zueva, VI Galkin, AR Cherkasov and RA Cherkasov (2002) Electronic Chemical Potential and Orbital Electronegativity of Univalent Substituents. Russian J Org Chem 38: 624-631.

73. RG Parr, LV Szentpály and S Liu (1999) Electrophilicity Index. J Am Chem Soc 121: 1922-1924.

74. PK Chattaraj, U Sarkar and DR Roy (2006) Electrophilicity Index. Chem Rev 106: 2065-2091.

75. PK Chattaraj and DR Roy (2007) Update 1 of: Electrophilicity Index Chem Rev 107: 46-47.