

TRANSPORT PROPERTIES OF SOME NEW THIADIAZOLE SCHIFF-BASE COMPLEXES

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Abstract

The samples under investigation were prepared by the conversional method where pure analar chemical (BDH) were used. FTIR were performed to assure the preparation of the samples in the proper form. The real and imaginary parts of the dielectric constant were measured for the different samples at different temperature as a function of the applied frequency. The obtained data were interpreted in view of the polarization mechanism and the ionic radii of the different metals used. The increase in the transition point with frequency means that the frequency acts as a pumping force pushing the change carriers from one conduction state to another. The addition of more than one element of different ionic radii affect directly on the physical properties because at certain radius some of these ions do not enter the structure.

Introduction

There is an intensive development in the syntheses of new derivatives of thiadiazole complexes designed for uses ranging from routine to sophisticated applications ⁽¹⁾. Various series of thiadiazoles and their metal complexes annelated derivatives are reported to have diverse biological activities as antibacterial ⁽²⁾, antimicrobial ⁽³⁻⁵⁾, antifirinolytic and anti-inflammatory ⁽⁶⁾, antihistamine agents and muscarinic agonists ⁽⁷⁾. In addition, some thiadiazole derivatives are useful as inhibitors of the neutral endopeptidase ⁽⁸⁾ carbonic anhydrase ⁽⁹⁾ anticarcenogenic ⁽¹⁰⁾ and kainic acid neurocytotoxicity ⁽¹¹⁾. Also, some substituted thiadiazoles are used as inhibitor for copper ⁽¹²⁾, complexing agent for Hg⁽¹³⁾ as well as additives to improve the properties of many lubricating greases and oils⁽¹⁴⁾. Recently, bis (compounds) attracted the attention of a large group of authors due to their successful utility as bulding units for many chain polymers ⁽¹⁵⁾. The biological activity of natural and synthetic compounds such as those under investigation increases as the molecular symmetry increases ⁽¹⁶⁾. This is based on the above facts and with continuation of our interest in the synthesis of novel bis-heterocycles ⁽¹⁷⁾.

In the present work one of our goals is to synthesis of some new metal complexes of thiadiazole Schiff- base as well as novel Co(II), Ni(II) and Cu(II) ⁽¹⁸⁾ Zcomplexes of intermediates for the synthesis of some new complexes of heterocycles. Also one of our targets is to improve the properties of these complexes through the measurement of the dielectric properties, schematic diagram for the prepared sample is shown in Fig.(1).

Experimental Techniques:

The melting points of the investigated samples were determined using electrothermal apparatus. IR spectra were recorded using KBr disk on a Bruker, vector 22, Germany or a Shimadzu FTIR 8201 PC spectrophotometer. Compounds (II)⁽¹⁹⁾, (III)⁽²⁰⁾, (IV)⁽²¹⁾ were prepared as previously reported ⁽¹⁾. The m. P and IR for the present samples where carried out in order to assure the formation of the samples in the proper form.

Synthesis of 2, 3-Dihydro-1, 3, 4-thiadiazole:

To a stirred solution of the appropriate hydrazonyl chloride (IV) (0.1 mole) in ethanol (20ml) triethylamine (0.1mole) was prepared and added in drops at room temperature and the reaction mixture was further stirred for two hours until it begins to precipitate. The precipitate was collected and crystallizes from acetic acid to give 2, 3 –Dihydro -1,3,4–thiadiazole as yellow crystals (90%) with m.p.219-220°C.

Preparation of the solid metal complexes:

A solution of the metal salt in 50 ml absolute ethanol was added drop wise to a solution of 2, 3 –Dihydro -1, 3, 4 -thiadiazole Schiff-base ligand (V) in 100 ml absolute ethanol at room temperature with continuous stirring. After the complete addition of the metal salt solution, the reaction mixture was heated under reflux for three hours. The reaction mixture was evaporated to give solid compounds. Recrystallization from ethanol was carried out to obtain the products (VIa-d). The analytical data of both aligned and its metal complexes are listed in table (1).

IR Spectra:

The IR spectra of the four complexes are shown in Figures (8-11) and listed in table (3). The similarity between IR spectra of different complexes is clearly observed. The strong bands that are most likely attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ ⁽²²⁾. Where is the band at $\nu(\text{C}=\text{O})$ is shifted towards lower wavenumber by (35-60) cm^{-1} in the tetranuclear complexes, indicating coordination of the carbonyl groups to the M(II) ions where is M(II) is Co(II), Ni(II) and Cu(II). The broad bands centered at 1085-1100 and 3465-3434 cm^{-1} is usually related to presence of phenyl and O-H respectively ⁽²³⁾. In the IR specrum of legend, bands due to $-\text{CH}=\text{N}-$ at 1566 cm^{-1} are also shift to lower side in complexation and it also indicates the formation of metal-nitrogen-sulfur bond. Due to the formation of new bonds, another new bands appeared in the low frequency region for (M-S) at 477-420 cm^{-1} and (M-N) at 615-580 cm^{-1} ⁽²⁴⁾.

Results and Discussion:

Figure (2) correlates the real part of dielectric constant ϵ' and absolute temperature at three different applied frequencies for the Ni^{2+} complexes. The data in the figure showed that nearly stable values of ϵ' with both temperature and frequency were obtained except a small hump was appeared at 360K the small hump at 360K can be ascribed to the structural variation of nickel complex. So it can be considered as thermochromic phase transition at which a reversible color change with temperature was observed. This hump appeared clearly in the inset of the figure also, this hump is due to phase transition that occurs in the sample. The stable region extended up to temperature of about 460K after which ϵ' increases drastically with absolute temperature. The splitting of the curves for different frequencies is very clear in the last region (high temperature). At the point of sharp increasing of ϵ' which vary from one frequency to another one can say that the polrizability is changed from very small value to a very large value due to participation of another types of polarization. This point was observed clearly in the conductivity data. From a closer look to the data it is clear that, at room temperature up to 460K the thermal energy is very small and can not free the localized dipoles with the result of very small polarizability as well as the dielectric constant. In the second region of temperature, the thermal energy is quite sufficient to liberate more dipoles and the applied electric field aligned them in its direction.

Figure (3) illustrates the dependence of the dielectric loss factor ϵ'' on the absolute temperature as a function of the applied frequency for Ni^{2+} complex. The effect of frequency was appeared very clear in the figure, where the transition point varies from one frequency to another. The temperature effect appears in a form of decreasing the internal viscosity of the sample which increases the friction between the dipoles and also increases the heat dissipation inside the sample. The result of this process appears in a form of increasing ϵ'' suddenly. The increase in the transition point with frequency means that, the frequency acts as a pumping force. In other word, it affects the ionization potential where its value for $\text{Ni}^{2+} = (176\text{kJ/mole})$ which lies between 178kJ/mole for Cu^{2+} and 186KJ/mole for Co^{2+} . The inset of this figure shows also the appearance of another transition temperature at about 400K .

Figure (4) shows the relations between ϵ' and absolute temperature at different frequencies for Co^{2+} complex. From the figure it is observed that the values of ϵ' in case of Co^{2+} is less than that of Ni^{2+} complex at the corresponding temperature. This can be ascribed to the electronic configuration of each element as well as the hydrogen bonding. When comparing the first transition temperatures of Ni^{2+} and Co^{2+} complexes one can find that its value for Ni^{2+} is greater than that of Co^{2+} complex. This can be attributed to the absorption coefficient of the two complexes which is directly correlated to the reversible color change of the sample with temperature. The dependence of ϵ'' on the absolute temperature at different frequencies for Co^{2+} complexes is shown in Fig. (4). the sudden increase in ϵ'' value can be attributed to the change in ionic radius from Cu^{2+} to Co^{2+} the probability of friction between dipoles decreases with the result of decreasing ϵ'' values and vice versa.

From a closer look to fig.(5) one can find that a thermochromic transition was appeared at about 311K as in the inset of fig.(4) and another transition at about 470K was obtained and assigned as chain melting transition where the sample still undecomposed at this chain melting points. The degrees of freedom become also large due to decreasing internal viscosity of the sampels. This leads to a large value of thermal energy dissipation inside the sample. Accordingly ϵ'' is increased reaching to a maximum value. In this case the electric field effect will aligned these charges in its direction. The dependency of ϵ' on the absolute temperature as a function of

frequency for Cu^{2+} complex is shown in Fig.(6). Nearly same trend as that of Co^{2+} is obtained with small shift in the transition temperature. The only difference is the larger values of ϵ' in case of Cu^{2+} complex than those of Co^{2+} complex. This may be due to more than one factor, the first one is the electronic distribution of each element and the second is the ionization potentials of Co^{2+} and Cu^{2+} ions which is responsible for the polarization as well as the dielectric constant. As a general trend of solid samples specially those with semiconducting properties such as those under investigations. The decrease in dielectric constant with increasing frequency is due to the fast variation of the field accompanied with the applied frequency where the dipoles can not follow it.

Figure (7) correlates the dielectric loss factor ϵ'' and absolute temperature for the Cu^{2+} complex. The data in the figure show that, there is a dispersion due to frequency. The appearance of the two transition temperatures, one at about 375K which gives a clear color change with temperature and it is called thermochromic transition and the second transition takes place after 440K which is at relatively high temperature with no shift in the transition point.

The values of the activation energy were calculated from the experimental results and reported in table (2). From the reported data, it is clear that, the activation energy decreases gradually with increasing the ionic radius which was expected result ⁽²⁵⁾. In other words bridging between the different ions in the layer becomes easier with increasing ionic radius leading to a decrease in the resistivity as well as the activation energy ⁽²⁶⁾. This enhances the results respected in table (2).

Conclusion:

The metal complexes of the formula $\text{C}_{50}\text{H}_{44}\text{N}_4\text{S}_2\text{M}(\text{L}_2\text{M})$ where $\text{M} = \text{Co(II)}$, Ni(II) and Cu(II) give more than one transition temperature, one of them is the thermochromic transition and the other is the chain melting transition ⁽²⁷⁾. The variation on the transition temperature depends on the electronic configuration of each element and on the ionization potential. The variation of the activation energy depends also on the above two factors. Over all, the obtained values of activation energy indicate the semi conducting like behavior of these complexes.

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Table (1): Elemental analyses, yields, colour, and melting points of the ligand and its corresponding metal complexes.

Compound No. M. F. (M. Wt)	Elemental analyses found (Calc.), %			Yield %	Colour	m.p. ^o C
	N	S	M			
V C ₂₂ H ₁₈ N ₂ O ₂ S (406)	6.25 (6.89)	7.80 (7.88)	--- ---	85.0	Yellow	219
VI C ₄₄ H ₃₆ N ₄ O ₄ S ₂ Co (870.9)	6.32 (6.43)	7.00 (7.34)	6.73 (6.76)	80.5	Light brown	266
VI C ₄₄ H ₃₆ N ₄ O ₄ S ₂ Ni (870.71)	6.40 (6.43)	7.32 (7.35)	6.73 (6.74)	84.0	Buff	270
VI C ₄₄ H ₃₆ N ₄ O ₄ S ₂ Cu (875.5)	6.35 (6.39)	7.30 (7.31)	7.00 (7.25)	87.0	Brown	>360

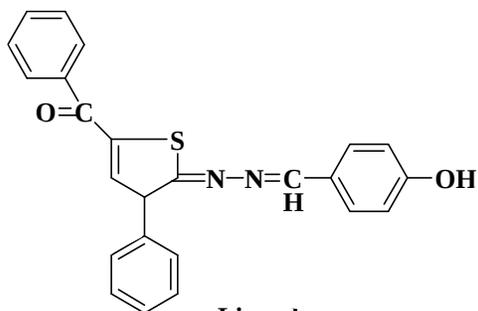
Table (2): Values of the activation energy in the low (E_I) and high (E_{II}) temperature regions at different metal elements.

Element in the complex	Activation Energy eV	
	E _I (e.V)	E _{II} (e.V)
Cu ⁺²	0.45	0.60
Ni ⁺²	0.33	0.72
Co ⁺²	0.28	0.74

Table (3): IR spectral data for the ligand and its metal complexes (cm⁻¹)

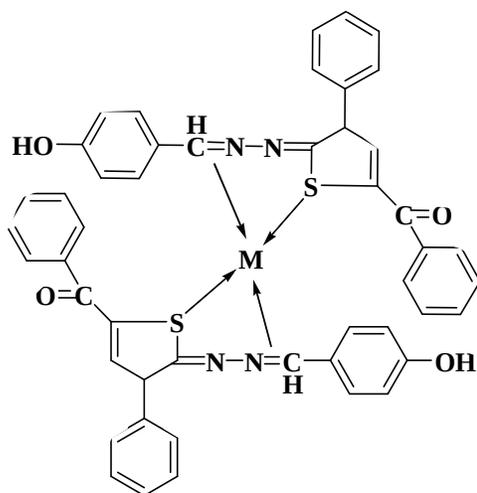
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Compound	ν (O-H)	ν (C=O)	ν (C=N)	ν (M-N)	ν (M-S)
Ligand	3443	1602	1566	---	---
Co(II)	3444	1566	1537	615	465
Ni(II)	3434	1567	1539	605	420
Cu(II)	3465	1539	1510	580	477



Ligand

Formula $C_{24}H_{18}N_2O_2S$ (L)



Complexes

Formula $C_{50}H_{44}N_4O_4S_2M$ (L_2M)
 where M= Co (II), Ni (II), Cu (II) and Zn (II).

Fig (1) Schematic diagram for samples

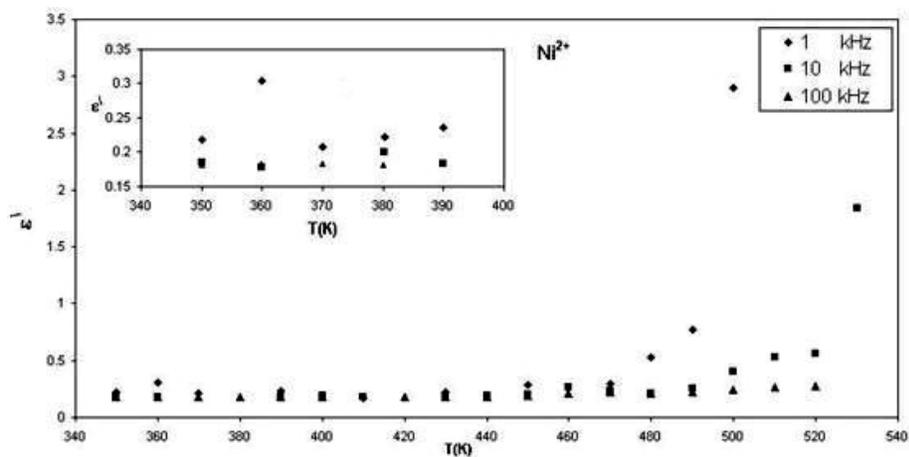


Fig (2) relation between the dielectric constant (ϵ') at three selected frequencies and absolute temperature for the complex containing Ni +2 ions

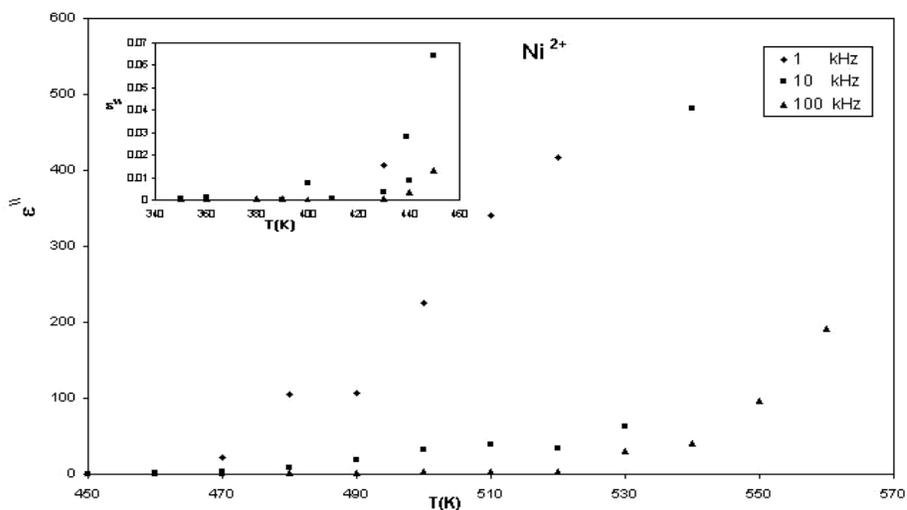


Fig.(3) relation between the dielectric loss factors (ϵ'') at three values of frequencies and absolute temperature for the complex containing Ni +2 ions

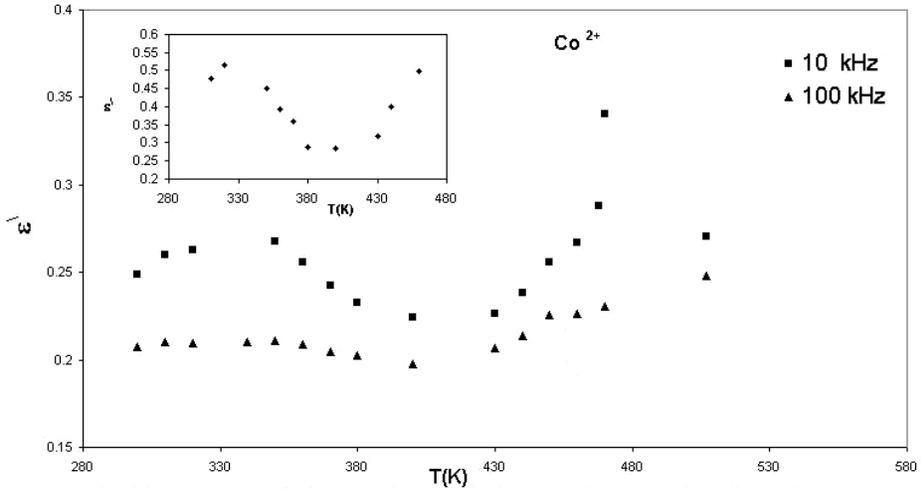


Fig (4) relation between the dielectric constant (ϵ') at two selected frequencies and absolute temperature for the complex containing Co +2 ions

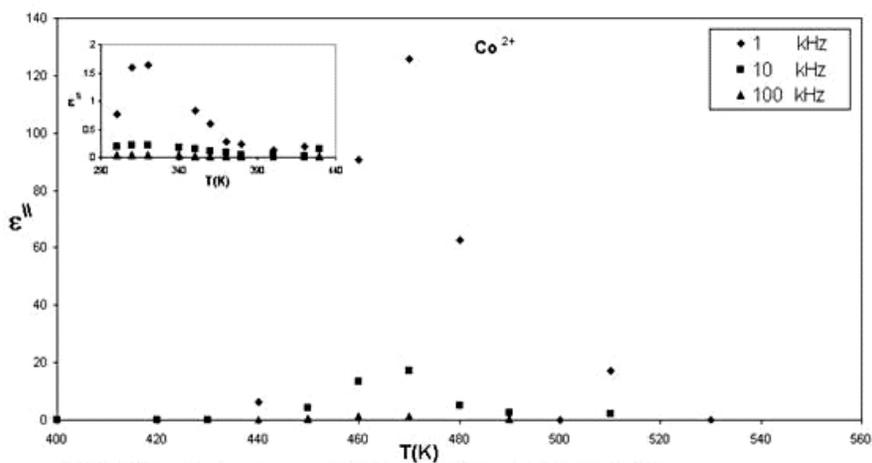


Fig (5) relation between the dielectric loss factors (ϵ'') at three values of frequencies and absolute temperature for the complex containing Co^{+2} ions

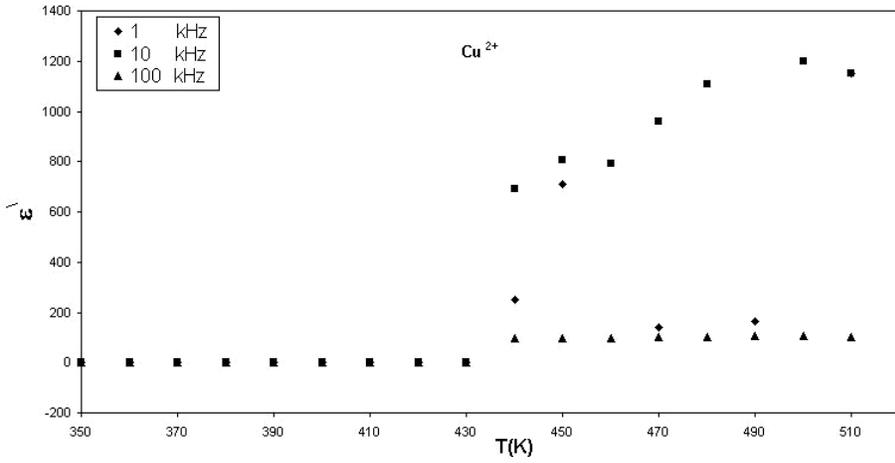


Fig.(6) relation between the dielectric constant (ϵ') at three selected frequencies and absolute temperature for the complex containing Cu +2 ions

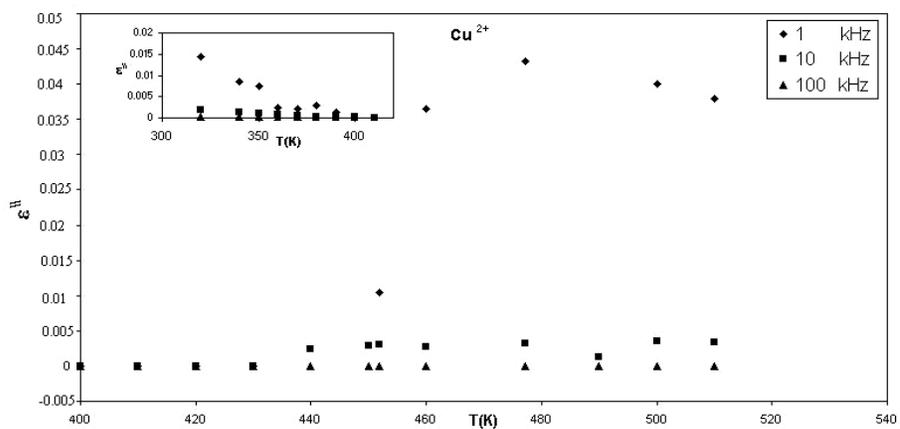


Fig.(7) relation between the dielectric loss factors (ϵ'') at three values of frequencies and absolute temperature for the complex containing Cu +2 ions

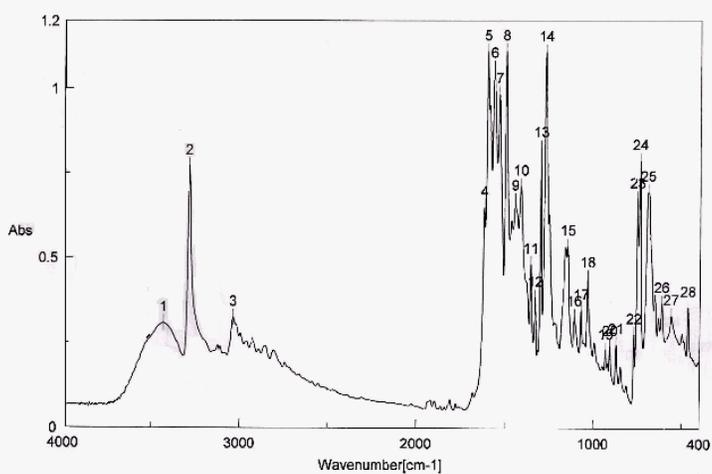


Fig. (8)

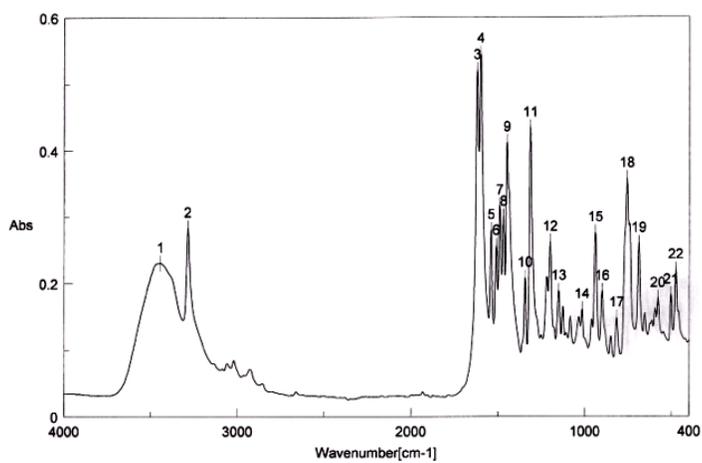


Fig. (9)

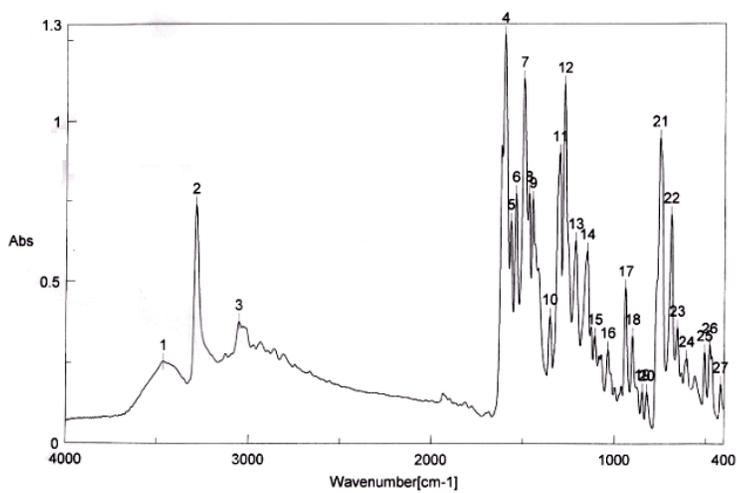
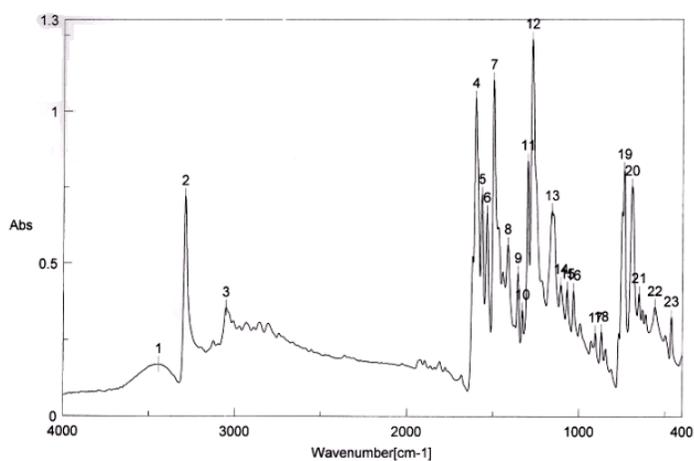


Fig. (10)

**Fig. (11)****References**

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