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Preparation of some tetrapyrizinoporphyrazine complexes of Zinc and Iron and study of some of their thermal, spectroscopic and electrical properties

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Abstract:

Zinc(II) and Iron(II) complexes of octaphenyltetrapyrizinoporphyrazine were prepared, identified and characterized . A study of their thermal, spectroscopic and electrical properties shows the relative thermal stability, effect of solvents on the electronic and the special dc electrical properties.

1. Introduction :

Tetrapyrizinoporphyrazines are compounds analogues of phthalocyanines in which eight nitrogen atoms occupy 1,4,8,11,15,18,22,25-position replacing the eight carbon atoms of the four benzene rings of the phthalocyanines. These compounds have unique properties and are used for different fields [1,2] .

Porphyrines were first structurally characterized by R. P. Linstead 1937 [3]. These compounds differ from those of phthalocyanines by their physical properties (colour, stability, and oxidation potential) [4,5] aggregation, solubility, IR, U.V-Visible spectra and other properties [6] .

The interaction of these molecules with the hetero atoms of different solvent molecules make it easily soluble in such solvents [7] such as, pyridine, DMF and DMSO [8].

The aggregation properties of these compounds might be attributed to the interaction of π - systems [9] . This property is not desirable because it reduces the solubility and causes some purification difficulties, and limitation of their applications [10,11,2] .

In this work a complexes of octaphenyltetrapyrizinoporphyrazine with Zn and Fe as central metal atoms were prepared and characterized by CHN, IR, U.V-Visible, TG and DTA. The dc electrical properties and the effect of different solvents on the electronic spectra for the prepared compounds were studied.

2. Experimental Section :

2.1. Materials :

Chemicals were purchased and used as received. Ethanol, acetone and chloroform

were purchased from GCC. Zinc acetate and HCl were purchased from BDH. HAc

were purchased from RDH. Quinoline, pyridine, diaminomalonitril(DAMN), urea and iron sulfate were purchased from

Fluka and hexanol was purchased from Merck.

2.2. Instrumentation:

The elemental analysis were recorded on Euro Vector EA3000A Italy. The IR spectra were recorded on FT- IR – 8400S. The UV-Visible spectra were recorded on T80-UV/Vis spectrometer. The H NMR(500MHz) spectra were recorded on Bruker. The TG and DTA were recorded on TGA–PL England in the temperature range (25-600)°C.

The dc electrical conductivity measurements were performed using an

electrical circle containing power supply(Leybold Heraeus) and heating plate(TJLASSO) and avometer (DT890). They were carried out using two types of cells, surfaces (cell constant 500 cm⁻¹) and sandwich (cell constant 0.01414 cm⁻¹). The cells were prepared by casting a concentrated solution of any of the compounds in chloroform on smooth and well cleaned aluminum surfaces (as electrode(s)).

2.3. Preparation of Compounds :

preparation of 2,3-dicyano 5,6-diphenyl 1) pyrazine (PN) [12] :

A mixture of (1g , 4.7×10⁻³ mole) of benzil, 25 ml of ethanol and 25 drops of acetic acid was put in a round bottomed flask filled with condenser containing (0.5 g , 4.6×10⁻³ mol) of DAMN soluble in 25ml ethanol. The total mixture was then refluxed for 4 hours. The reaction mixture then left for two days to complete the precipitation. The solid product then filtered and recrystallized from a mixture of hexanol and acetone (1:1). The product was a pale yellowish crystalline powder, (m.p = 253-255 °C) (yield, 0.7g, 52%).

IR (KBr): (3055w, 1600s, 1520vs, 1070m, 700vs, 1375vs and 2235m)cm⁻¹.
H NMR(δ H, ppm): (7.38, 7.46, 7.54).

2) preparation of 2,3,9,10,16,17,23,24-octaphenyl 1,4,8,11,15,18,22,25 –

octaphenyltetrapyrazinoporphyrazine zinc (II) OpPzZn [13]:

Zinc (II) actate (0.2 g , 1.09×10⁻³ mole) was added to a solution of PN(1.23g, 4.3× 10⁻³ mole) in 3 ml of quinoline followed by the addition (1.5 gm , 2.5×10⁻² mole) urea, The mixture then heated at 140°C for 10 minutes with magnetic stirring. The reaction mixture then cooled, and dissolved in a least amount of chloroform and the reprecipitated by ethanol. This procedur was repeated for five

times, and then dried at 120 °C ,The product is a greenish powder (yield,0.26g, 20%).

CHN, calcd (C₇₂H₄₀N₁₆Zn) C: 72.39, H: 3.35 , N: 18.76; found C:71.81, H: 3.61, N: 18.65; IR(KBr): (3056w, 1649m, 1523s, 1161s, 773vs, 1357vs and 1245m) cm⁻¹.
UV-Vis(λ_{max} ,CHCl₃): (310,630 nm). H NMR (δ H, ppm): (7.38, 7.47 and 7.52) .

3) preparation of 2,3,9,10,16,17,23,24 - octa (phenyl) 1,4,8,11,15,18,22,25 – octaazaphthocyani- natoiron (II) OpPzFe [13] :

Iron(II)sulfate(0.2 g, 1.3×10⁻³ mole) was added to a solution of (1.47g, 5.2× 10⁻³ mole) of PN dissolved in 3 ml of quinoline, followed by the addition of (1.5 g, 2.5×10⁻² mole) of urea. The mixture then heated at 140°C for 15 minutes with magnetic stirring. The reaction mixture then cooled, and dissolved in a least amount of chloroform and the reprecipitated by ethanol. This proceed was repeated for five times, and then dried at 120 °C . The product is a deep brown powder, (yield, 0.4g, 25%).

CHN, calcd (C₇₂H₄₀N₁₆Fe) C: 72.98, H: 3.37, N: 18.92; found C: 71.84, H: 3.38, N: 19.89. IR (KBr): (3064w, 1633m, 1559s, 1188m, 773vs, 1375vs, 1247s) cm⁻¹. UV-Vis (λ_{max} ,CHCl₃): (300,654 nm). H-NMR (δ H, ppm): (7.38, 7.46, 7.54).

3. Result and Discussion :

3.1. Spectroscopic results

The little differences of the practical with the calculated elemental percentage in the CHN analysis might be due to the difficulties of purification of such compounds.

The IR spectra, figures (1-3) show the aromatic C-H stretching at 3055cm^{-1} , 3056cm^{-1} and 3064cm^{-1} for PN, Zn and Fe complexes respectively and the aromatic C-H bending at 1070cm^{-1} , 1188cm^{-1} and 1161cm^{-1} in plane for PN, Zn and Fe complexes respectively, and 773cm^{-1} for C-H out of plane for the Zn complex.

The bands 1375cm^{-1} , 1600cm^{-1} and 2235cm^{-1} for PN is attributed to the stretchy vibration for C-N, C=N and the C≡N stretchy vibration respectively [14-16]. The bands at 1649cm^{-1} and 1633cm^{-1} for the Zn and Fe complexes which are attributed to the C=N stretching

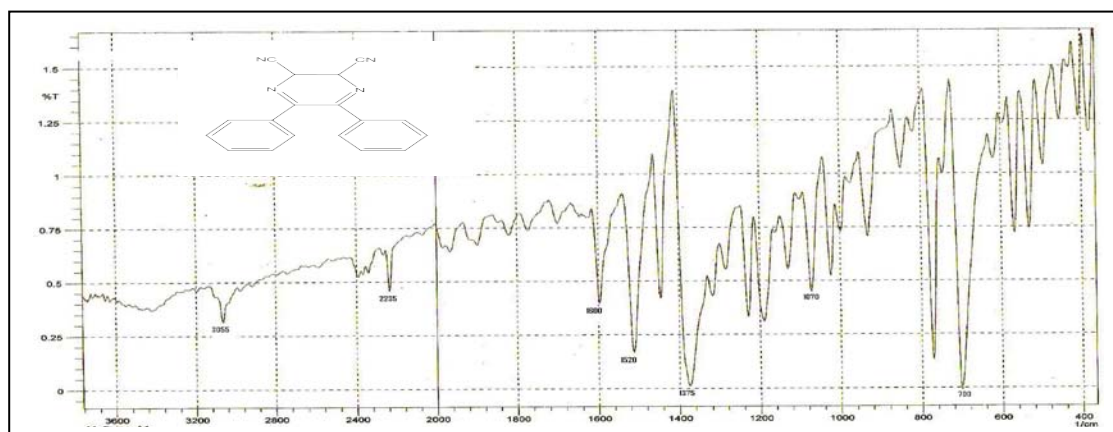


Figure (1): The IR spectrum for PN

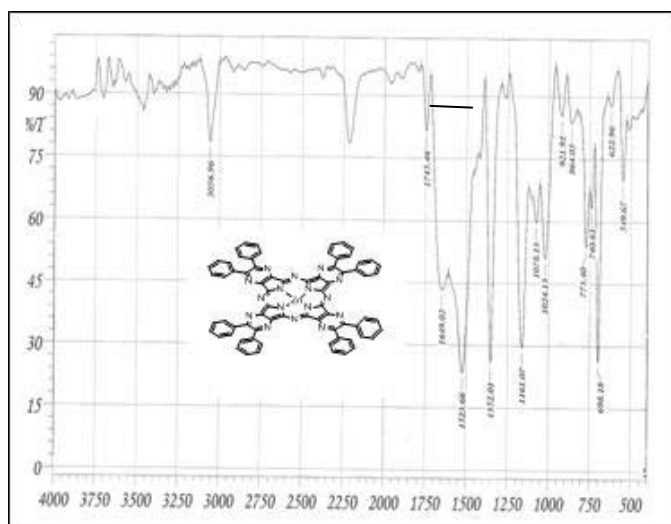


Figure (2): The IR spectrum of

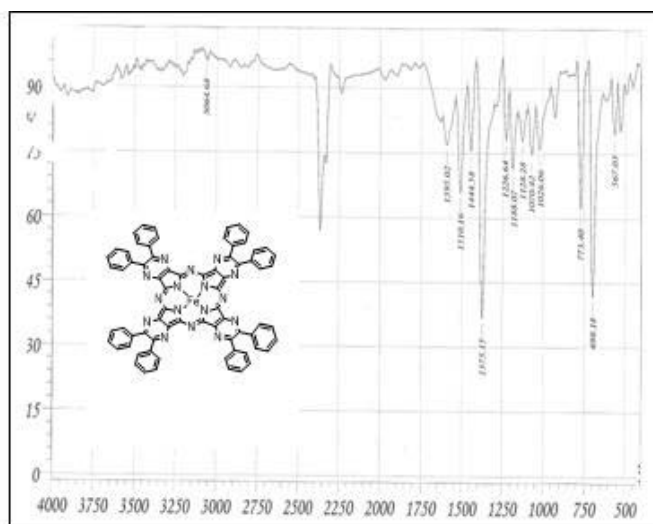


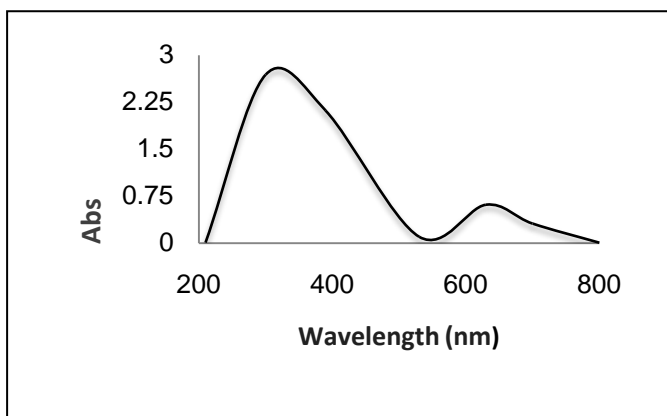
Figure (3): The IR spectrum of

The U.V-Visible spectra figures (4) and (5), show the main two band types, the Q band at 630 nm and 656 nm and the soret band at 310 nm and 300 nm (soret band) for Zn and Fe complexes respectively, Which could be attributed to the $(\pi-\pi^*)$ transitions

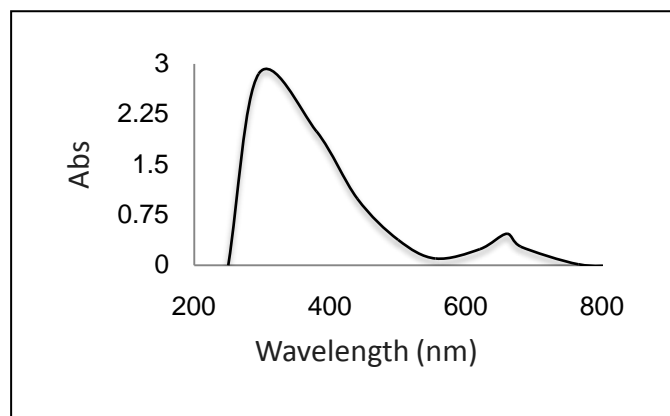
in addition to the coupling of electrons of the nitrogen atoms to the π -system [17].

For comparison, figure(6) shows the electronic spectrum for the starting compound (PN) in chloroform (10^{-4}M). It shows a three bands at 244 nm, 272 nm and

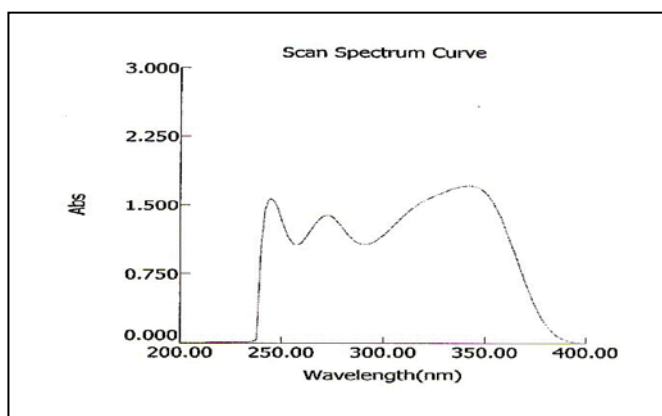
342 nm which are related to $\pi - \pi^*$ transition[12].



Figure(4) : The U.V-Visible for OpPzZn



Figure(5) : The U.V-Visible for OpPzFe



Figure(6) : The U.V-Visible for PN

The H- NMR spectra for PN, figure (7), shows a mixed band at 7.5 ppm which is related to the benzene protons. It appears by higher resolution as two triplets at 7.38 ppm and 7.46 ppm and doublet at 7.54 ppm

which is attributed to the meta, para and ortho protons, respectively[18]. The band of the solvent (CDCl_3) appears at 7.24 ppm. (figure (8)).

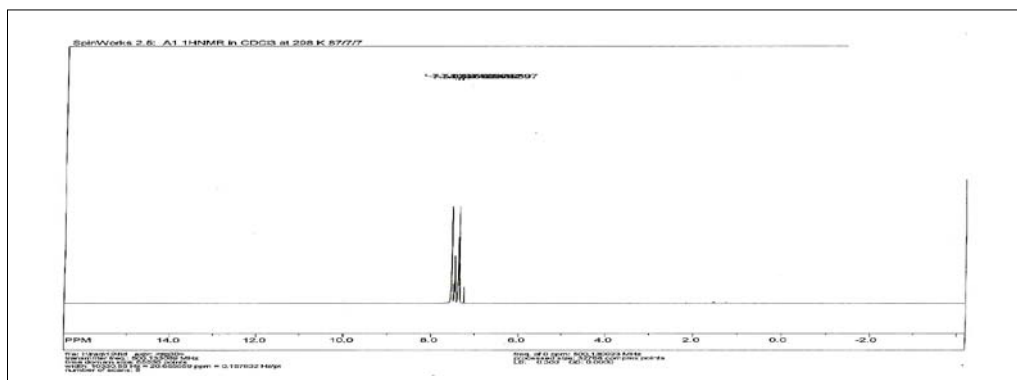


Figure (7): The H- NMR spectrum for PN

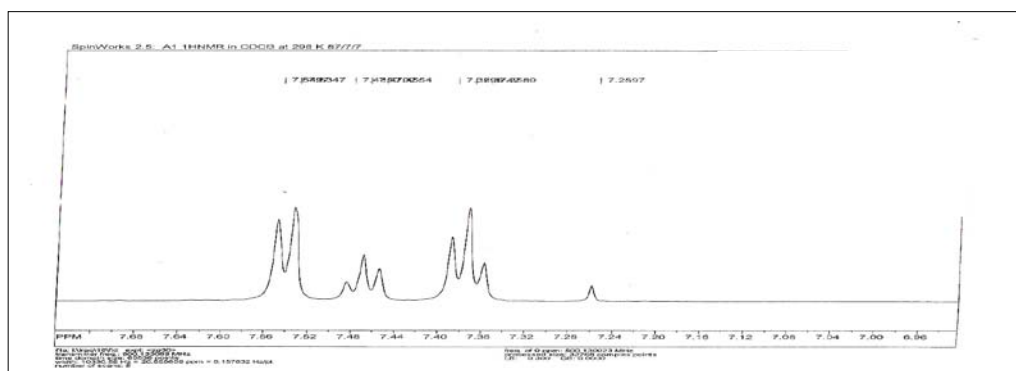


Figure (8): The H-NMR spectrum of PN with higher resolution

The H-NMR spectrum, figure (9), shows a mixed band centred at 7.4 ppm for the Zn complex which could be attributed to the benzene protons, while the peaks at 2.4 ppm and 3.3 ppm are attributed to the solvent DMSO and absorbed water respectively [18],

while figure (10) shows the spectrum for Fe complex, The spectrum shows a mixed band centred at 7.5 ppm which could be attributed to the benzene protons, The peak at 7.26 ppm is attributed to the solvent CDCl_3 .

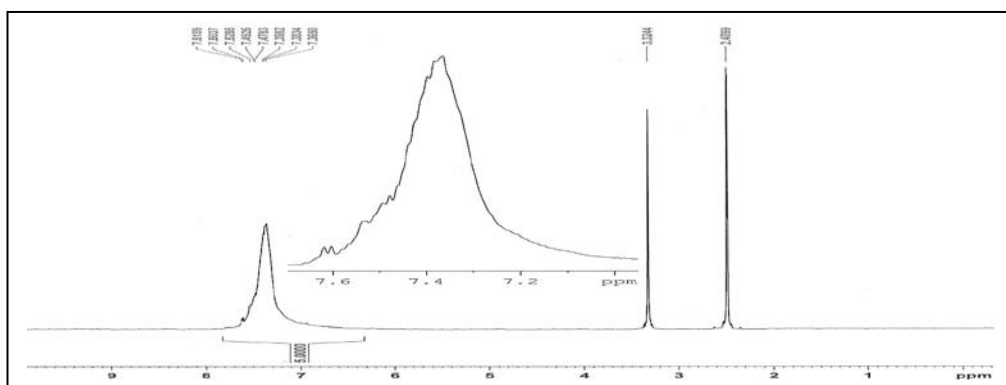
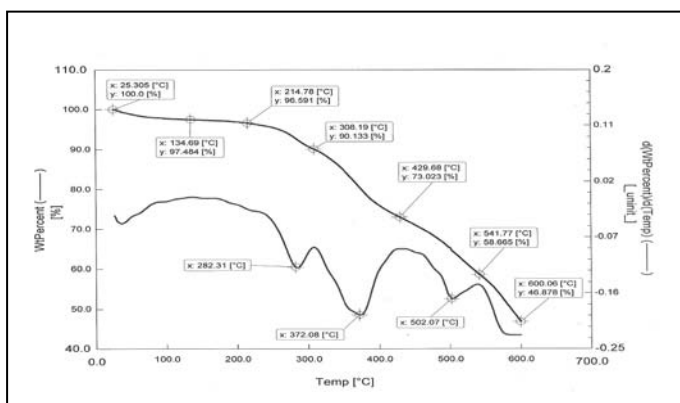
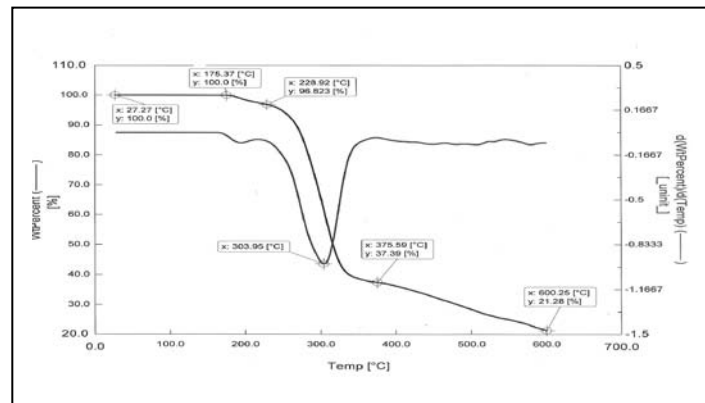


Figure (9): The H-NMR spectrum for OpPzZn



Figure(11) : The TG and DTA for OpPzZn



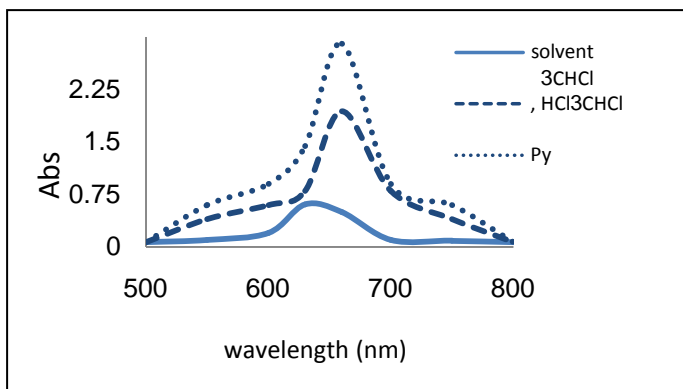
Figure(12) : The TG and DTA for OpPzFe

3.4. Effect of Solvents:

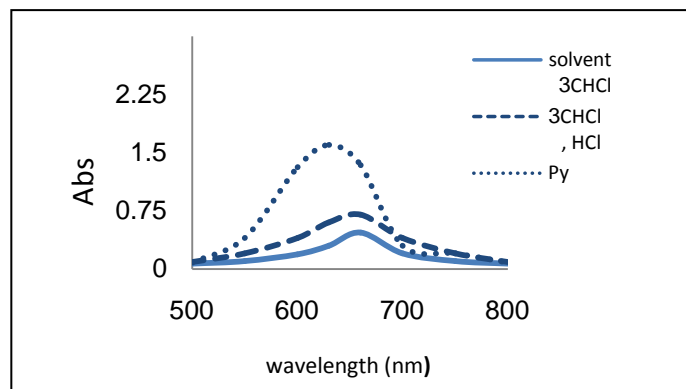
Figures (13) and (14) show the U.V-Visible spectra for the Zn and Fe complex, ($1 \times 10^{-4} M$) in chloroform, chloroform with acid (HCl) (0.6M), and in pyridine.

The figures show a single and wide peaks at 656, 630 nm for the Fe and Zn complexes respectively. The width of the peaks refers to the low symmetry and to the aggregation of the molecules [19] .

These peaks become higher and thinner at 675nm with the use of acidic chloroform, which relate to the higher symmetry with less aggregation. In pyridine the peaks become higher and extra thinner which is due to the higher polarity of pyridine which could make extra coordination with the central metal atoms that reduce the aggregation [20,21] .



Figure(13) : The effect of solvents on the U.V-Visible spectra of OpPzZn



Figure(14) : The effect of solvents on the U.V-Visible spectra of OpPzFe

3.5. D.C Electrical Conductivity:

The studied electrical conductivity of the prepared compounds (Zn and Fe complexes) as surface and sandwich cells are shown in the figures (15 – 20).

Figures (15) and (16) show the relation of the flowing current with time. During the first period the relation is exponential and the current reached to a constant value after 10 minutes for both complexes and for both

surface and sandwich cells while the sandwich cell of the Fe complex reaches a constant value after nearly 5 minutes. The decrease in the conductivity with time might be due to the evaporation of some solvent molecules and displacement of some of the complex molecules which might change the order of the crystal structure [22] .

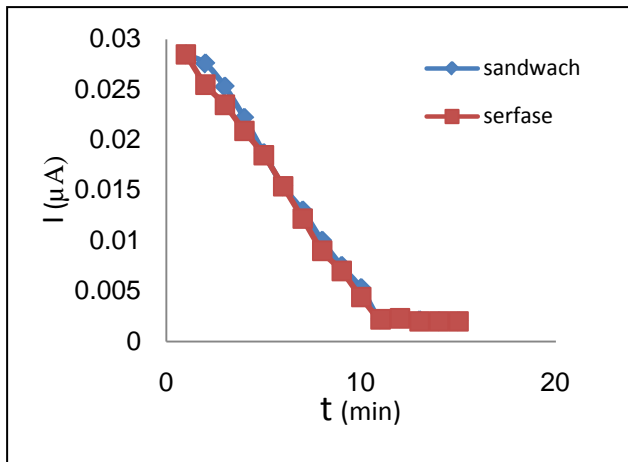


Figure (15): The relation of the current flow with time for both kinds of cells for OpPzZn at 7 volts

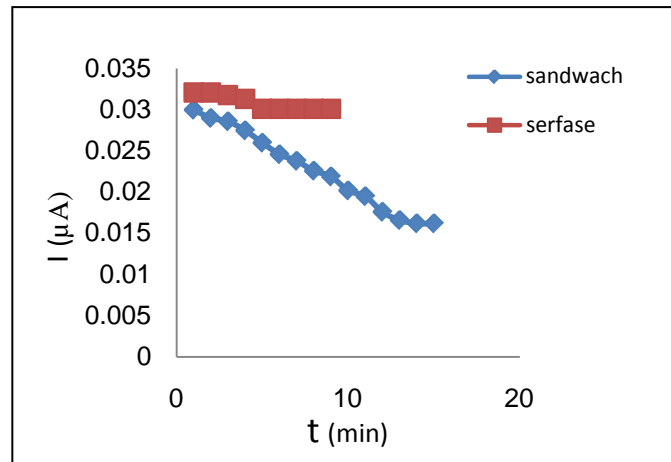


Figure (16): The relation of the current flow with time for both kinds of cells for OpPzFe at 7 volts

Figures (17) and (18) show a current voltage relation, for both complexes and

both kind of cells. The figures show an ohmic relation in the range with in 10 volts.

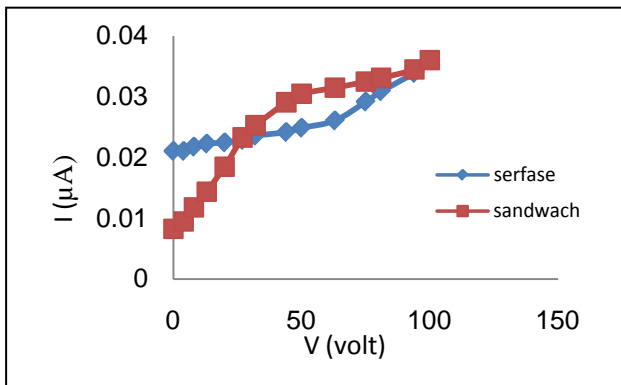


Figure (17): The current voltage relation for both kinds of cells for OpPzZn.

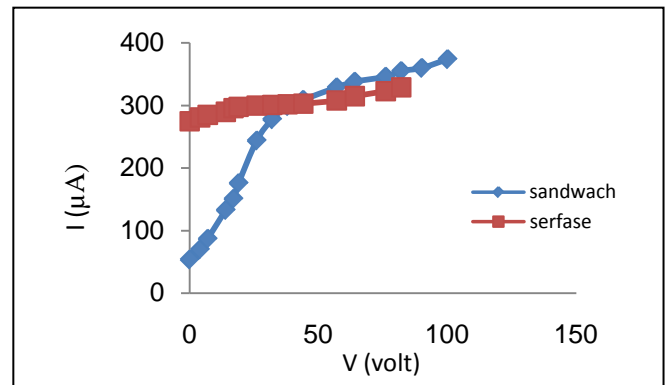


Figure (18): The current voltage relation for both kinds of cells for OpPzFe.

Figures (19) and (20) show the relation between the conductivity with temperature, and the natural logarithm of conductivity and the reverse temperature respectively according to the relation $\sigma = \sigma_0 \exp(-\Delta E / kT)$, where σ and σ_0 are the conductivity and the pre-exponential conductivity respectively. ΔE is the band gap. K and T are the Boltzmann constant and the

temperature in Kelvin. The figures show that the conductivity increase with temperature till it reaches a highest value then it began to decrease. The decrease in conductivity might be due to a decrease in the crystal structure order which increases the crystal disorder. The disorder was found by other works[23].

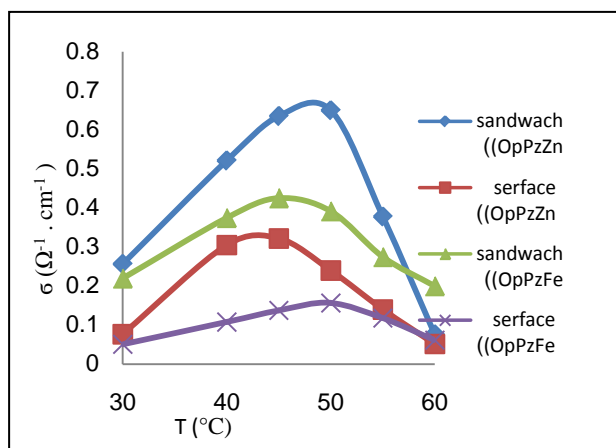


Figure (19): The relation between the conductivity and temperature for both kinds cells.

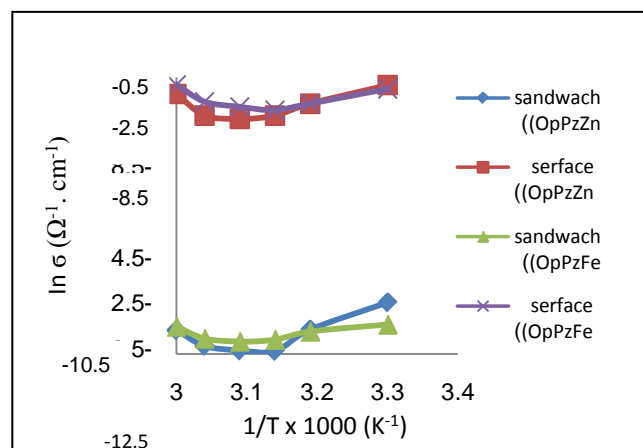


Figure (20): The relation between the pre-exponential conductivity and reverse temperature for both kinds cells

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