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TRANSPORT MECHANISM IN Zn DOPED POLYANILINE CONDUCTING POLYMER

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ABSTRACT: *The present work includes a study on the transport mechanism in Zn doped polyaniline conducting polymer. PANI is one of the most conducting polymer in which the transition takes place between migration of proton and polaron.*
The yield of PANI was higher than 90% in all cases. The doping element was $ZnCl_2$. The synthesized sample of PANI has been characterized by using FTIR (Fourier Transform Infrared) Spectroscopy and IR, DC electrical conductivity is measured for knowing the conduction mechanism. We have measured DC electrical conductivity of each sample at different temperature. The plot of log σ verses 1/T is linear for all $ZnCl_2$ doped sample. The activation energy is estimated from this plot and found to be 0.1956 eV for 0.274 vol fraction of $ZnCl_2$ sample. The structure characterization is studied via FTIR and found have maximum peak value 3672.47cm^{-1} indicate the O-H type of stretching. We have measured DC electrical conductivity of each sample and thickness.

KEYWORDS: *PANI,FTIR,IR, Polymer, Monomer, Doped.*

I. INTRODUCTION

PANI is one of the most studied materials because of its high conductivity on doping with acid, well behaved electrochemistry and easily prepared under reproducible condition by both electro polymerization and chemical oxidation of aniline, chemical and electrical stability and good environmental stability.

PANI is oxidative product of aniline under acidic condition and is known in 1862 as aniline black.Conducting polymer a great deals of researches have been devoted to PANI due to its unique electrical, electrochemical properties, high environmental stability, easy polymerization and low cost of monomer.

Concentration and functional group present in PANI is detected by the FTIR spectroscopy .FTIR spectra polyaniline have been taken by using Perkin Elmer Spectrometer for the structural characterization FTIR is an important physical tool. The IR spectroscopy is one the most powerfull analytical technique it provides the usefull information about the structure of the molecule and bonding quicklywithout tired some evaluation method. FTIR provides very faster of identifying the chemical structure is specially those of the organic ones. This device generates Fourier Transform of the IR spectrum which is converted to the spectrum itself by the computer. IR gives information on the vibrational and rotational modes of motion of molecule and hence an important technique for identification and characterization of functional group. The IR of an organic compound provide unique figure prints which is readily distinguished from the absorption pattern of all other compound.

1.1 Synthesis:

PANI was prepared by chemical oxidation of 0.2 M aniline sulfate with 0.25 M ammonium peroxydisulfate according to literature procedure. Aniline sulfate was dissolved in distilled water in volumetric flask to 50 ml of solution .Ammonium peroxydisulfate was dissolved in water also to 50 ml of solution .both solution were then mixed in a beaker and then add the doping material ZnCl2 in the 100 ml distilled water and take out 2 ml, 4ml, 6ml, 8ml, 10ml solution and doped it in standard solution briefly stirred and left at rest to polymerize for 24 hours. The green precipitate was collected on a filter, washed with 100 ml portions of acetone, to removes the low molecular weight organic intermediates and oligomers. Polyaniline hydrochloride was dried in air.

II MEASUREMENT OF DC ELECTRICAL CONDUCTIVITY

Sample is placed in sample holder for electrical measurement .sample holder is placed in furnace firstly. The temperature of furnace is set at room temperature. Voltage across the sample was kept constant about 5V .the current was measured by digital picometer at different temperature. The temperature was measured by digital thermometer. These measurement were made in the temperature range 40-110^{0}C

2.1. Observation Table -1:

Area of cross section(A): 0.785cm^2, Voltage:- 5V (Same for all fractions)
For 2ml $ZnCl_2$ doped
For 0.274vol.fraction of $ZnCl_2$ pallet
Thickness (t):- 0.1033cm

Temp(T) ^{0}K	1/T K^{-1}	Current(I) Amp	R_S=Rt-1X10^6	Conductivity σ=t/R_sA (Ωcm)$^{-1}$	LOG(σ) (Ωcm)$^{-1}$
373	0.002681	1.18E-06	3.23E+06	4.07E-08	-7.3899
368	0.002717	1.16E-06	3.30E+06	3.99E-08	-7.3986
363	0.002755	1.13E-06	3.44E+06	3.82E-08	-7.4178
358	0.002793	1.02E-06	3.89E+06	3.38E-08	-7.4704
353	0.002833	8.72E-07	4.73E+06	2.7E-08	-7.5559
348	0.002874	7.90E-07	5.33E+06	2.47E-08	-7.6074
343	0.002915	6.81E-07	6.34E+06	2.07E-08	-7.6830
338	0.002959	5.50E-07	8.09E+06	1.63E-08	-7.7887
333	0.003003	4.30E-07	1.06E+07	1.24E-08	-7.9072
328	0.003049	3.21E-07	1.46E+07	9.03E-09	-8.0444
323	0.003096	2.01E-07	2.39E+07	5.51E-09	-8.2587
318	0.003145	1.78E-07	2.71E+07	4.86e-09	-8.3135
313	0.003195	1.05E-07	4.66E+07	2.82E-09	-8.5493

For 4ml $ZnCl_2$ doped
For 0.548vol.fraction of $ZnCl_2$ Pallet
Thickness (t):- 0.1042cm

Temp(T) ^{0}K	1/T K^{-1}	Current(I) Amp	R_S=Rt-1X10^6	Conductivity σ=t/R_sA (Ωcm)$^{-1}$	LOG(σ) (Ωcm)$^{-1}$
373	0.002681	1.49E-06	2.36E+06	5.63E-08	-7.2491
368	0.002717	1.45E-06	2.45E+06	5.43E-08	-7.2654
363	0.002755	1.32E-06	2.79E+06	4.76E-08	-7.3222
358	0.002793	1.25E-06	3.00E+06	4.42E-08	-7.3541
353	0.002833	1.11E-06	3.51E+06	3.78E-08	-7.4221
348	0.002874	1.01E-06	3.98E+06	3.34E-08	-7.4763
343	0.002915	9.21E-07	4.43E+06	3.00E-08	-7.5232
338	0.002959	8.25E-07	5.06E+06	2.62E-08	-7.5812
333	0.003003	7.03E-07	6.11E+06	2.17E-08	-7.6632
328	0.003049	6.12E-07	7.17E+06	1.85E-08	-7.7325
323	0.003096	6.00E-07	7.33E+06	1.81E-08	-7.7423
318	0.003145	5.15E-07	8.71E+06	1.52E-08	-7.8169
313	0.003195	4.28E-07	1.07E+07	1.24E-08	-7.9056

For 6ml $ZnCl_2$ doped
For 0.822vol.fraction of $ZnCl_2$ Pallet
Thickness (t):- 0.1086cm

Temp(T) ^{0}K	1/T K^{-1}	Current(I) Amp	R_S=Rt-1X10^6	Conductivity σ=t/R_sA (Ωcm)$^{-1}$	LOG(σ) (Ωcm)$^{-1}$
373	0.002681	1.38E-06	2.62E+06	5.29E-08	-7.2766
368	0.0027174	1.36E-06	2.68E+06	5.17E-08	-7.2866
363	0.0027548	1.33E-06	2.76E+06	5.01E-08	-7.2998
358	0.0027933	1.24E-06	3.03E+06	4.56E-08	-7.3408
353	0.0028329	1.17E-06	3.29E+06	4.20E-08	-7.3765
348	0.0028736	1.10E-06	3.54E+06	3.91E-08	-7.4077
343	0.029155	1.04E-06	3.82E+06	3.62E-08	-7.4413

338	0.0029586	9.10E-07	4.49E+06	3.08E-08	-7.5117
333	0.003003	8.23E-07	5.08E+06	2.73E-08	-7.5645
328	0.0030488	7.45E-07	5.71E+06	2.42E-08	-7.6158
323	0.003096	6.02E-07	5.31E+06	1.89E-08	-7.7227
318	0.0031447	4.35E-07	1.05E+07	1.32E-08	-7.8799
313	0.0031949	3.08E-07	1.52E+07	9.08E-09	-8.0419

For 8ml $ZnCl_2$ doped
For 1.096vol.fraction of $ZnCl_2$ Pallet

Thickness (t):- 0.1223cm

Temp(T) ^{0}K	1/T K^{-1}	Current(I) Amp	R_S=Rt-1X10^6	Conductivity σ=t/R_sA $(\Omega cm)^{-1}$	LOG(σ) $(\Omega cm)^{-1}$
373	0.002681	1.51E-06	2.32E+06	6.73E+08	-7.1721
368	0.002717	1.42E-06	2.52E+06	6.18E+08	-7.2090
363	0.002755	1.40E-06	2.57E+06	6.07E+08	-7.2167
358	0.002793	1.34E-06	2.75E+06	5.67E+08	-7.2460
353	0.002833	1.22E-06	3.09E+06	5.04E+08	-7.2976
348	0.002874	1.11E-06	3.51E+06	4.44E+08	-7.3525
343	0.002915	1.01E-06	3.95E+06	3.94E+08	-7.4040
338	0.002959	9.18E-07	4.45E+06	3.50E+08	-7.4554
333	0.003003	8.56E-07	4.84E+06	3.22E+08	-7.4923
328	0.003049	8.02E-07	5.23E+06	2.98E+08	-7.5263
323	0.003096	7.15E-07	5.99E+06	2.60E+08	-7.5850
318	0.003145	6.29E-07	6.95E+06	2.224E+08	-7.6493
313	0.003195	5.25E-07	8.52E+06	1.83E+08	-7.7380

For 10ml $ZnCl_2$ doped
For 1.37 vol.fraction of $ZnCl_2$ Pallet

Thickness (t):- 0.0989cm

Temp(T) ^{0}K	1/T K^{-1}	Current(I) Amp	R_S=Rt-1X10^6	Conductivity σ=t/R_s A $(\Omega cm)^{-1}$	LOG(σ) $(\Omega cm)^{-1}$
373	0.002681	1.49E-06	2.35E+06	5.36E-08	-7.2709
368	0.0027174	1.47E-06	2.41E+06	5.23E-08	-7.2818
363	0.0027548	1.35E-06	2.70E+06	4.66E-08	-7.3316
358	0.0027933	1.30E-06	2.85E+06	4.42E-08	-7.3548
353	0.0028329	1.26E-06	2.98E+06	4.23E-08	-7.3740
348	0.0028736	1.21E-06	3.14E+06	4.01E-08	-7.3969
343	0.0029155	1.19E-06	3.20E+06	3.94E-08	-7.4051
338	0.0029586	1.19E-06	3.22E+06	3.91E-08	-7.4075
333	0.003003	1.15E-06	3.336E+06	3.75E-08	-7.4259
328	0.0030488	1.06E-06	3.73E+06	3.38E-08	-7.4709
323	0.003096	8.56E-07	4.84E+06	2.60E-08	-7.5846
318	0.0031447	8.07E-07	5.20E+06	2.42E-08	-7.6153
313	0.0031949	7.12E-07	6.02E+06	2.09E-08	-7.6794

III RESULT AND DISCUSSION

The conductivity is given by formula

$\sigma = \sigma_0 \exp\left(\frac{\Delta E}{kT}\right)$

Where

σ is the conductivity at temperature T in ^{0}K

ΔE −is the activation energy.

$\sigma_0$is the pre –exponential factor.

k- is the Boltzmann constant=$1.38X10^{-23}JK^{-1}$

T- is the temperature in ^0K

The conduction is determine from resistance and dimension of the sample is follow

$$\sigma = \frac{t}{RA}$$

Where

T is thickness of the sample

A is the area of sample.

R is the resistance of the sample.

Figure 1 shows the plot of logσ verses 1/T for all samples of different compositions.

The variations of logσ verses 1/T is linear for all samples. The activation energy evaluated from the slop of line.

ΔE=slopeX K Joule

Where

K is the Boltzmann constant.

Activation energy is in eV

$\Delta E = \frac{\text{slopeX K}}{1.6X10-19}$ eV

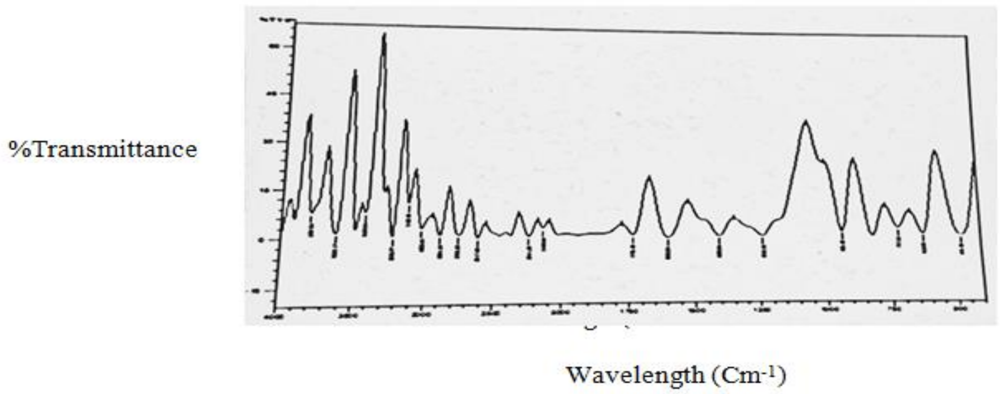
Thickness, diameter, area, conductivity, logσ , and temperature all the values for different compositions are included in table.

The conductivity of various samples is measured for temperature range 313K-373K. The value of DC conductivity with the temperature is reported in table 1.

The plot of logσ verses 1/T is linear for all $ZnCl_2$ dopped sample. The activation energy is estimated from this plot and found to be minimum 0.062 eV for 1.37 vol.fraction of $ZnCl_2$sample .

FTIR spectra for different concentration of $ZnCl_2$ doped:

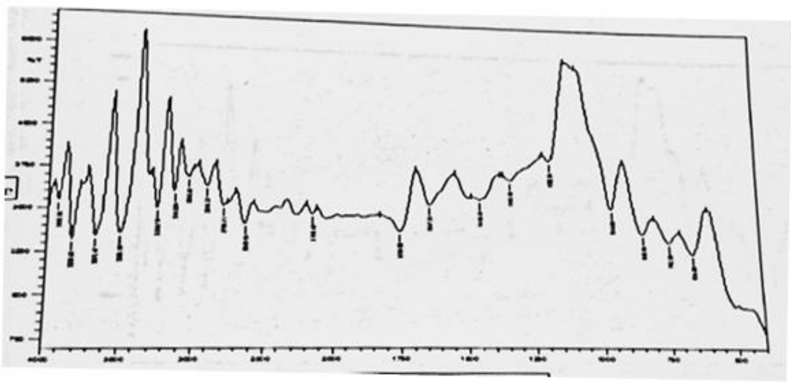
For 2ml $ZnCl_2$ doped :



Sr. No	Experimental Frequency	Molecular Motion	Functional group
1	655.80	C-H	Alkenes
2	742.59	C-H	Alkenes
3	840.16	C-H	Alkenes
4	956.69	C-H	Alkenes
5	1192.01	C-O	Alcohols, Ethers, Carboxylic acid, Esters
6	1342.46	C-O	Alcohols, Ethers, Carboxylic acid, Esters
7	1458.18	C-N	Amines
8	1647.21	N-H	Amines
9	3506.59	O-H	Hydrogen bonded alcohols, Phenols

For 4ml $ZnCl_2$ doped:

%Transmittance

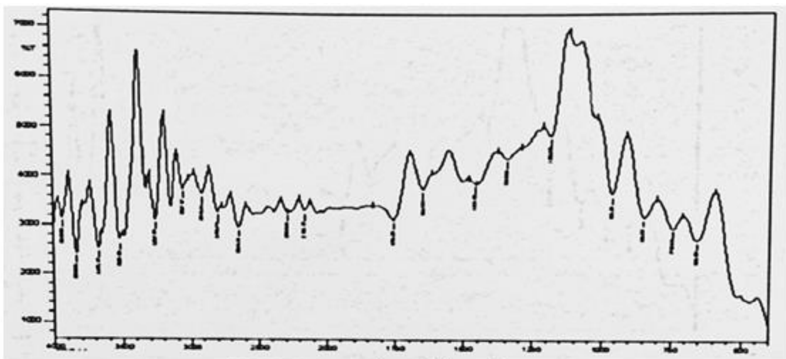


Wavelength (Cm^{-1})

Sr.No	Experimental Frequency	Molecular Motion	Functional group
1	623.01	C-H	Alkenes
2	717.52	C-H	Alkenes
3	935.48	C-H	Alkenes
4	1242.16	C-O	Alcohols, Ethers, Carboxylic acid, Esters
5	1408.04	C-N	Amines
6	1602.35	N-H	Amines
7	3423.17	O-H	Hydrogen bonded alcohols, Phenols

For 6ml $ZnCl_2$ doped:

%Tranmittance

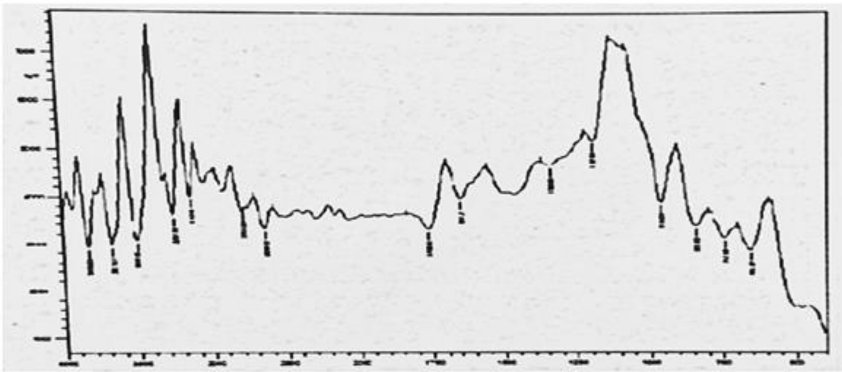


Wavelength(Cm^{-1})

Sr.No	Experimental Frequency	Molecular Motion	Functional group
1	655.80	C-H	Alkenes
2	742.59	C-H	Alkenes
3	839.03	C-H	Alkenes
4	956.69	C-H	Alkenes
5	1184.29	C-O	Alcohols ,Ethers, Carboxylic acid ,Esters
6	1340.53	C-O	Alcohols, Ethers, Carboxylic acid, Esters
7	1456.26	C-N	Amines
8	1647.21	N-H	Amines
9	3672.47	O-H	Hydrogen bonded alcohols, Phenols

For 8ml $ZnCl_2$doped :

%Tranmittance

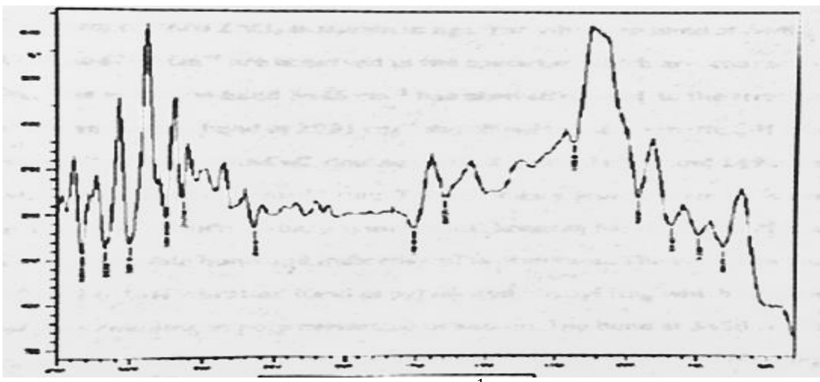


Wavelength(Cm^{-1})

Sr.No	Experimental Frequency	Molecular Motion	Functional group
1	653.87	C-H	Alkenes
2	742.59	C-H	Alkenes
3	839.03	C-H	Alkenes
4	956.69	C-H	Alkenes
5	1192.01	C-O	Alcohols ,Ethers ,Carboxylic acid ,Esters
6	1338.60	C-O	Alcohols ,Ethers ,Carboxylic acid ,Esters
7	1647.21	N-N	Amines
8	3506.59	O-H	Hydrogen bonded alcohols ,Phenols

For 10ml $ZnCl_2$ doped:

%Tranmittance



Wavelength(Cm^{-1})

Sr.No	Experimental Frequency	Molecular Motion	Functional group
1	655.80	C-H	Alkenes
2	742.59	C-H	Alkenes
3	839.03	C-H	Alkenes
4	956.69	C-H	Alkenes
5	1190.01	C-O	Alcohols ,Ethers ,Carboxylic acid ,Esters
6	1647.21	N-N	Amines
7	3506.59	O-H	Hydrogen bonded alcohols ,Phenols

Figure1:- Plot of LOG(σ) verses 1/T for various concentration

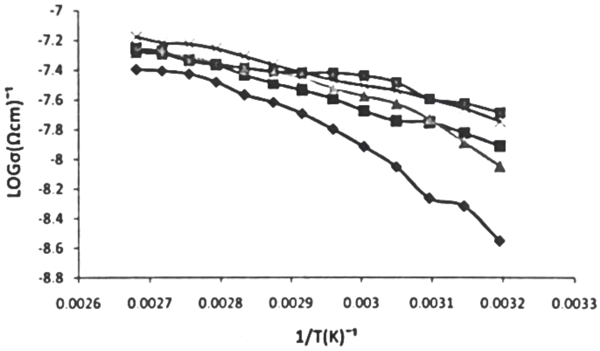


Figure2:- Plot of LOGσ_{RT} verses vol. fraction of $ZnCl_2$

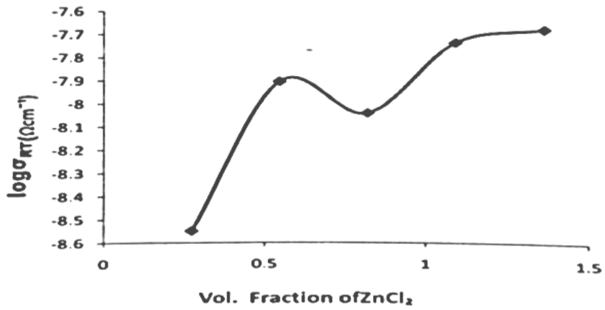
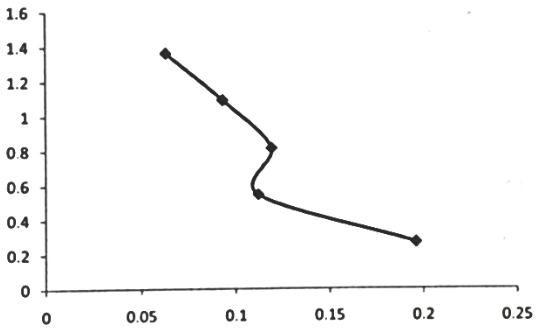


Figure3:- Plot of ΔE (eV) verses Vol. fraction of $ZnCl_2$

Vol. fraction of $ZnCl_2$



ΔE (eV)

IV CONCLUSION

From above figure2 it is clear that the LOGσ_{RT} changes as the vol. fraction of $ZnCl_2$ changes at room temperature(RT=313K) and figure3 it is clear that decrease in activation energy for increasing vol. fraction of $ZnCl_2$.

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