International Journal of Scientific Research in Chemical Sciences

Research Paper Volume-1, Issue-1 ISSN: 2455-3174

Spectroscopic Analysis of Conducting Polymeric Material

Dr. Anubha Vijay Pandya[1*] and Rati Trivedi Nair

1.Deptt.of Engg. Chemistry, Prestige Institute of Engg. & Science. Indore, (M.P.)

anubhavpandya@gmail.com,
2. Christian Eminent Academy of Management, Professional Education and Research Indore
prapti1611@gmail.com

Abstract – Spectroscopic analysis of conducting polymeric material helps to reveal valuable information about the complex formation of metal(Li,Zn,Al etc.)with ligand i.e. polymer(Polyaniline,Polyethylaniline,Polymetylaniline,Polypyrrolidone etc.).Various spectroscopic technics may be used in this manner such as Infra Red spectroscopy,X-ray Diffraction technich ,UltraViolet spectroscopy etc.In this paper Infra Red spectroscopy and X-ray Diffraction technich have been used to analyse the complexation and conducting behaviour of the polymeric material which can be used in rechargeable batteries.Infrared spectroscopy deals with various bands which correspond to the charecteristic functional groups and bonds present in polymeric substances .In other words Infrared spectoscopy has been used for assigning the binding sites in metal : polymer complexes.A critical comparision of the structurally important IR absorption bands of each polymer and that of its complexes with Zn(II) and Al (III) metal ion has been reported.

In the X-ray analysis of polymers the diffraction spots are board and diminish rapidly with increasing diffraction angle .X-ray spectroscopy, like optical spectroscopy is based upon measurement of emission absorption scattering fluorescence and diffraction of electromagnetic radiations. Such measurements provide much useful information about the composition and structure of matter[6,7,8] To study the structural properties of polymeric material X-ray diffraction measurements are performed through the interaction of X-ray the structure of the compound may be thoroughly investigated. The X-ray diffraction theory based on single crystals of low- molecular weight substances is not applicable in the explicit treatment of polymer samples. There are a few studies in this direction [9, 10, 11] X-ray diffraction formulas are sorted to kinds, A and B as follow_

(A) X-ray diffraction intensity by an infinitely large crystal.

(B) X-ray diffraction intensity by a finitely large crystal. X-ray studies of Polymers and their complexes have been done. On basis of X-ray diffractograms it is easy to explain the Composition and structure of polymeric samples. It is also possible to explain the increasing conductance of polymeric electrolytes.

X-ray diffraction method makes it possible to analyze the crystal structure of real crystallites which actually exists in synthetic fibers and plastics and thereby the structural property relation of polymer materials will be considered in more detail.

Keywords:- Polymeric Material, Complex, Polyaniline and Polyaniline-Zink complex

INTRODUCTION

Infrared spectroscopy is one of the most powerful analytical techniques which offers the possibility of chemical identification.This technique when coupled with intensity measurements may be used for quqntitative analysis .one of the most important advantages of infrared spectroscopy over the other usual methods of structural analysis such as X-ray diffraction analysis ,electron spin resonance etc. is that it provides useful information about the structure of compounds and can solve many problems in organic chemistry and coordination chemistry .In present paper ,with the help of Infrared spectroscopy conformation of polymer –metal complex formation has been assured that can help to study of polymer as conducting material to prepare polymer electrodes and polymer electrolytes .This research paper will help to prepare polymer batteries. For this purpose polymer,metal-polymer complex like Polyaniline and Polyaniline-Zink complex have been tested using KBr as reference material with the help of Infrared spectrophotometer.

The technique is based on the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations the molecule of a chemical substance vibrates at many rates of vibration ,giving rise to close packed absorption bands called an IR absorption spectrum which may extend over wide wavelength range. Various bands will be present in IR spectrum which will correspond to the characteristic

functional groups and bonds present in a chemical substance is a fingerprint for its identification .
In a complex polymer molecule the number of infrared transition might be expected tobe too great to deal with, but fortunately this does not happen as a great ,many of these are degenerate,i.e.of the same energy.the advantage of fingerprint region has been taken in the identification of polymers . The spectrum of the unknown sample is matched against that of an authentic sample, peak by peak , and the identity of the compound established .

IR Spectra of Polyaniline –original format

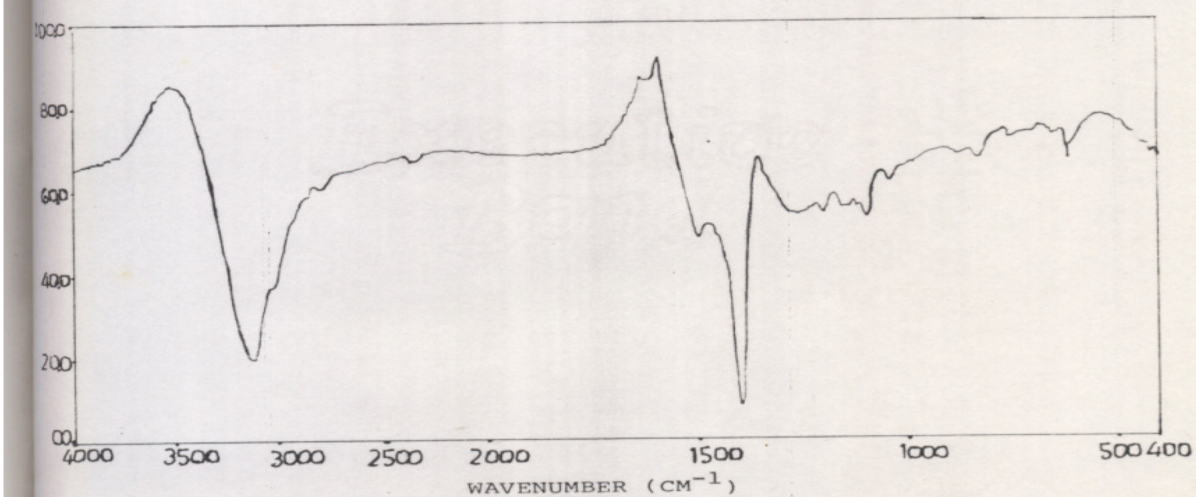

Fig.3.1 : IR spectrum of Polyaniline.

IR spectra of PANI-Zinc complex-original format

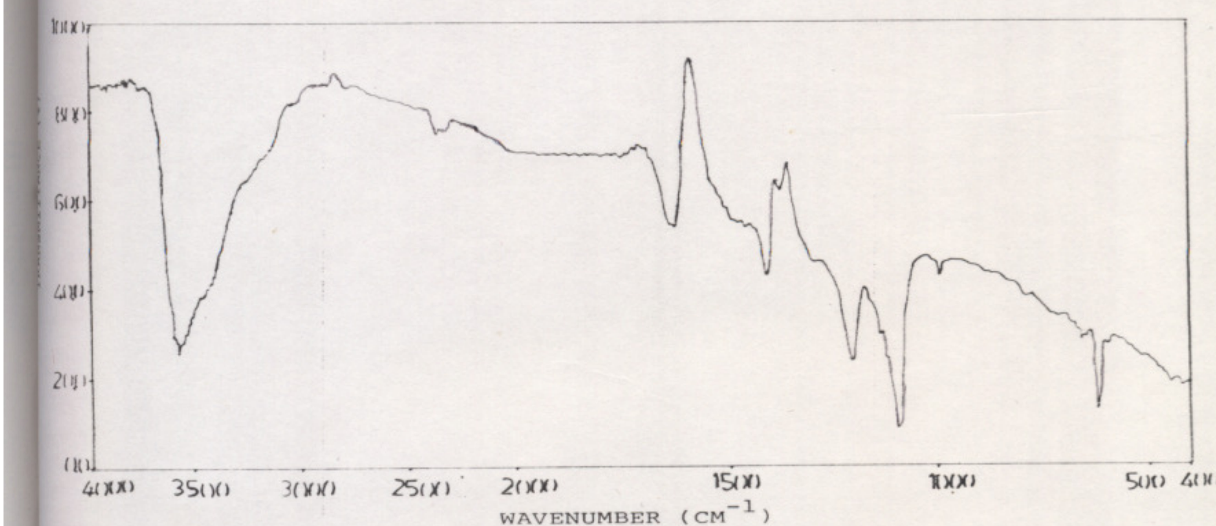

Fig.3.2 : IR spectrum of Zn(II)-Polyaniline complex.

Table- IR Frequencies (cm^{-1})and their assignments for PANI and its complex

Ligand	**assignment**	**Zn-(II)- PANI Complex**
3500 -I br	-NH stretching	3565
3300_I	vibration	
1600w	-C=C	1626
1500s	-NH-bending	
Aromatic nature	-	
1380 -I br	-C-N vibration	
1360_I	aromatic secondary	1402
amine		
1100m	CH in plane stretching	
780 -I br	CH bending	
620_I	vibration	619

s-sharp, m-medium ,w-weak , br-broad

In the past seven decade's X-ray diffraction and other derived techniques viz- .DPP, cyclic voltammetry etc.have gained popularity among the analytical scientists for the qualitative and quantitative analysis of almost all types of organic substances. X-ray diffraction measurements are performed through the interaction of X-ray the structure of the compound may be thoroughly investigated. The X-ray diffraction theory based on single crystals of low- molecular weight substances is not applicable in the explicit treatment of polymer samplesThe polarographic parameter i.e. half wave potential $E_{1/2}$ plays a vital role in the polarographic techniques. Since the half wave potential is the characteristic of the electro active species which helps to analyze the electro active species qualitatively and quantitatively. The temperature dependence of the polyaniline film voltammetric response in aqueous and non aqueous by Q.Inselt[4] He observed that only a very slight shift into the direction of more negative potentials (Ca-10 mV) and a small increase in the temperature is increased by 30^0C

Preparation of polymer complex –An adequate quantity of the polyaniline host and the inorganic salts of Zn were separately dissolved in suitable solvent (e.g. acetonitrile) the two solutions were then mixed and after stirring the solvent were slowly evaporated to finally obtain powder form of polymeric complexes. Polyaniline sulphate polymer sulphate was prepared by chemical method applying oxidant (Potassium dichromate) the polymerization of 0.4 moles of aniline in 1lit. of 1M sulphuric acid was affected using 1g equivalent of the potassium dichromate a precipitated was separated, washed, dried and weighed as polyaniline sulphate
Polyaniline Chloride was prepared by equilibrating the polyaniline sulphate with1M HCl for about 10hrs. The mass so obtained was separated, washed and dried and weighed as polyaniline Chloride

Table : X-ray Diffraction patterns for Polyaniline

Aluminium		**Zink**		**Polyaniline**		**Zinc-polyaniline**		**Aluminium-polyaniline**	
2θ	**d(A^0)**	**2θ**	**d(A^0)**	**2θ**	**d(A^0)**	**2θ**	**d(A^0)**	**2θ**	**d(A^0)**
38.45	**2.338**	**36.28**	**2.473**	**3**	**14.68**	**18.8**	**4.718**	**3**	**14.68**
44.7	**2.024**	**38.9**	**2.308**			**20.38**	**4.353**	**6.25**	**7.5**
65.10	**1.431**	**43.2**	**2.091**			**23.82**	**4.127**	**9**	**4.9**
69.19	**1.221**	**54.3**	**1.187**			**26.25**	**3.732**	**10.62**	**4.15**
						29.32	**3.392**		
						31.99	**3.043**		
						35.1	**2.795**		
						35.77	**2.554**		
						42.97	**2.508**		

X-ray Diffraction patterns for Polyaniline

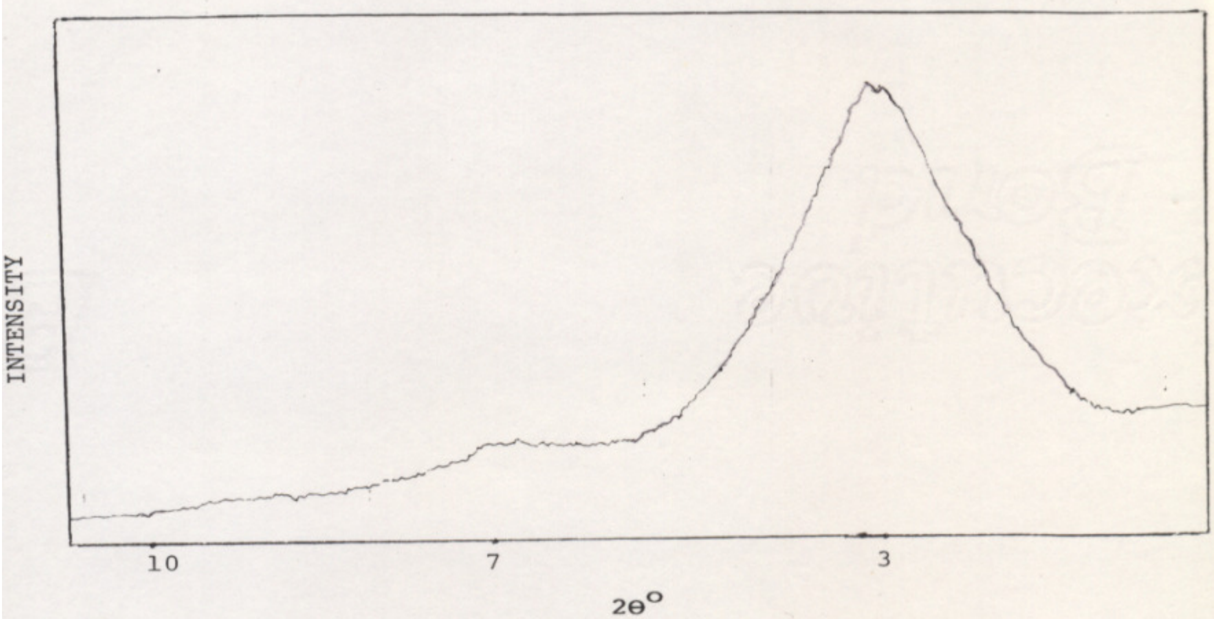

Fig. 4.1 : X-ray diffraction pattern for Polyaniline.

Experimental

The X- ray Diffraction studies on the polymers/electrolytes /electrodes were carried out using a RIGAKU X-Ray Diffractometer (Japan) . The X-ray beam was Nickle filtered Cu KX Radiation from a seald tube operated at 40 KV and 50mA.

All the Chemicals used were of anala R/BDH grade.

0.01 M metal (Zn^{++}) solutions were prepared by dissolving the requisite quantity of their soluble salts in double distilled water 0.1 M PANI solutions were prepared in small amount of hydrochloric acid diluted to required volume with distilled water.

Experimental sets of solutions containing overall concentration of supporting electrolyte (KCl) and Metal ion fixed at 0.1 M and 1.0 mM respectively. Whereas in other sets in addition to the above supporting electrolyte and metal ion concentration of each polymer (ligand) was varied . Polarograms were recorded on an ELICO (Hyderabad) pulse polarograph ModelCL-90 having a dropping mercury electrode (DME) a saturated calomel electrode (SCE) a working electrode as a working electrode reference electrode respectively. The DME had a characteristics of m=2.33 mgs^{-1} t=3.03at 40cm effective height of mercury column ,$m^{2/3}\ t^{1/6}$=2.13$mg^{2/3\ s-1/2}$

Survey of literature –

W.John Albery[3], et.al have used electrode such as polyaniline, polypyrol and polythiophene. They showed that the behavior of the different polymers is similar and may be explained by a chemical model involving localized redox species with two possible conformations of the polymer.

The temperature dependence of the polyaniline film voltammetric response in aqueous and non aqueous media has been investigated by G.Inzelt[2] .He observed that only a very slight shift into the direction of more negative potentials in the peak potentials (Ca -10mv) and a small increase in the peak current as the temperature is increased by 30^0C.

Youn Chaol on Park Yong Woo studied behaviour Polyaniline and found that the electrons are moving in and out changing the polyaniline structure from one form to the another form

C. Herold 12 Yazmi, DBillaud attempted study of sodium doped polyparaphenylene film,
John Alberry, et.al

Result and Discussion-

IR Spectra of Polyaniline and its complex with Zink (II)metal ion has been depicted in figure . The important Infrared signal and their group assignments have been tabulated in table
A perusal of the figure and table reveals that the signals due to NH-stretching vibrations at 3500-3300cm^{-1} and –CN aromatic vibration in the ligand spectra undergoes a shift in the spectrum of Zn(II)-PANI complex indicating the involvement of –NH nitrogen complex formation.

X-ray diffraction method makes it possible to analyze the crystal structure of real crystallites which actually exists in synthetic fibers and plastics and thereby the structural property relation of polymer materials will be considered in more detail. On the basis of X-ray diffractograms it is easy to explain the Composition and structure of polymeric samples. It is also possible to explain the increasing conductance of polymeric electrolytes. X-ray diffraction measurements are performed through the interaction of X-ray the structure of the compound may be thoroughly investigated. The X-ray diffraction theory based on single crystals of low-molecular weight substances is not applicable in the explicit treatment of polymer samples.

References –

[1]. J.Lingane,Chem.Rev.,29,1(**1941**)
[2]. Youn Chaol on ,Park yong Woo. Hanguk Multi.Hakh-oechl,Ungyong Mulli, 2(3), 256-60(Korean)(**1989**).
[3]. C. Herold ,R.Yazami,D.Billaud,Terre (France)
[4]. W.John Albery, Zheng Chem., Benjamin R.Horrocks, Andrew R. Mount and Peter. J.Wilson, David Bloor Andew T. Monkmann ,C.Michal Elliot ,Fabradar Chem. Soc.88, 247-259(**1989**)
[5]. Bruno Scrosati, solid state ionic devices, 18-23 July 131-133(**1988**)
[6]. H.A. Liebhatsky,H.G. Preiffer,E.H.Winslow and P.D.Zemany,X-Rays,Electrons and Analytical Chemistry John Wiley and Sons (NewYork), (**1972**).
[7]. Bertin EP, Introduction to X-ray Spectrometric Analysis, Plenum press (NewYork), (**1978**).
[8]. R. Jenkins, R. W. Gouid and D. Gedeke,Quantitative X-ray spectrometry marcel Dekker, (NewYork),(1981).
[9]. L.G. Wallner, Monatsh, Chem 79, 86 (**1948**).
[10]. L.G. Wallner, Monatsh, Chem 79, 279 (**1948**).
[11]. B.K. Vainshtein, Diffraction of X-ray by chain Molecules ,Eisovier, Amsterodam, 257 (**1966**).
[12]. K. Kaji and I. J. Sakuraka, Polym. Sci. ,Polym Phys.,Ed. 12,1491(**1974**).

