

Studies of transition metal ion - 5- Sulphosalicylic acid doped Polyanilines

N. Muneeswaran

Abstract: Metal ion-5-sulphosalicylic acid (5-SSA) complexes were used as dopant for Emeraldine base to prepare high spin polyaniline metal composites. The so prepared emeraldine salts were characterized by FT-IR, magnetic susceptibility, conductivity, X-ray diffraction (XRD) and Surface electron microscopy (SEM) studies in order to understand the influence of functionalized dopants on the physico-chemical properties of polyaniline. The conductivity was increased on increasing the concentration of metal ion complexes. Magnetic measurements showed a negative magnetic susceptibility (χ_g) value for 5-sulphosalicylic acid doped polyaniline while positive magnetic susceptibility (χ_e) values were found for the transition metal ion doped polyanilines. XRD study showed that the polymers are in amorphous state and it contained metal ions. Surface electron microscope analysis showed that the morphological structure of the doped polyaniline had small grain particles with particle sizes varied from 10 – 500 μm s.

Key words: polyaniline; metal ions; 5- Sulphosalicylic acid; d.c-magnetic susceptibility; d.c-conductivity; FT-IR; SEM studies.

I. Introduction

Metal containing polymer composites have attracted the attention of scientific community over a last few decades. Insertion of metal ions into polymer backbone may improve the mechanic, electronic and magnetic properties of polymer [1]. Among the conducting polymers, Polyaniline is considered because of its easy synthesis, low cost, good environmental stability, and easy solution processing etc., [2, 3, 4]. Polyaniline exists in different discrete oxidation states which are called as leuco-emeraldine, emeraldine base and pernigraniline (Fig.1). All these forms are insulators. Only the protonated form of polymer system can show metallic conductivity. Recently it is shown that conjugation length in conducting polyaniline is around 30 \AA and it is dependent on the disorder created [5, 6, 7]. Many reports on PANi containing metal ions are known from the literature. PANi-TiO₂ composite annotates [7], Films of PANi-V₂O₅ [8], PANi-Silica composites [9], Inclusions MoO₃ into PANi structure [10], PANi doped with gold nanoparticles [11], PANi prepared by molten salts [12], PANi coated electrodes containing Fe (CN)₆^{3/4-} [13], FeCl₃ doped PANi [14], and electrochemical incorporations of copper into Polyaniline layers [15]. Polyaniline- metal oxalate composites [16] are reported. PANi- Fe₂O₃ composites are reported by Meixiang Wan group [17]. Tang et al used Mahemite to dope Polyaniline in the presence of anionic surfactant [18]. The deformation in the molecules occurs with co-ordination of metal atom to PANi chain and this leads to complex formation [19, 20, 21]. The doping of emeraldine base with PdCl₂ yielded Pd – PANi and it exhibited the catalytic properties in the hydrogenation of 2-ethyl anthraquinone [22, 23, 24] and in the hydrogenation of Hexyne to hexane (24). Li⁺ ion is next mostly studied inorganic metal ions [25]. In this experiment, Mn⁺², Fe⁺², Co⁺², Ni⁺² and Cu⁺² are used as dopants in aqueous medium to polyaniline to understand the effect of dopants on various physico-chemical properties of polyaniline. The results are presented and discussed in the present study.

II. Experimental

The transition metal ion such as Mn⁺², Fe⁺², Co⁺², Ni⁺² or Cu⁺² will react with 5-sulphosalicylic acid to give 5-sulphosalicylato-tetra aqua complexes or bis-5-sulphosalicylato diaqua complexes [26]. Equimolar quantities of aqueous solutions of transition metal carbonate and 5-sulphosalicylic acid are mixed in the stoichiometric ratio and heated at 50 °C on a heating mantle to prepare these complexes. The so prepared complexes are used to dope Polyaniline in aqueous medium. Emeraldine base form of polyaniline is synthesized according to known procedure. Doping experiments are carried out using 1.82 g of emeraldine base (0.01 mole) with 100 ml of doping solution by stirring them nearly three hours to achieve maximum doping. The doped polymer is filtered and dried under vacuum for 24 hours. The various concentrations of metal carbonate, the various concentrations of metal carbonate with various concentration of 5- sulphosalicylic acid are used as doping solutions. The exact concentrations of metal complex of 5 – sulphosalicylic acids are collected in Table – 1. The structures of polyaniline – metal composites are characterized by FT-IR, magnetic susceptibility, conductivity, X-ray diffraction and SEM studies. IR transmittance spectra are taken on Perkin Elmer Paragon – 500 FT-IR spectrometer in KBr pellets in the range 4000 to 400 cm^{-1} . X-ray diffraction (XRD) measurements are made with a computer controlled XRD unit model JEOL-JDX 8030 using CuK α radiation ($\lambda=1.5418 \text{\AA}$).

Magnetic susceptibility is measured by Guoy balance at room temperature. $\text{HgCo}(\text{SCN})_4$ is used as the calibrant. The electrical conductivity of the pressed pellet of the compounds are measured by standard four probe method at room temperature using a Keithley model 2400 series source meter and Keithley model 2182 Nano voltmeter equipment. The Surface electron microscopy (SEM) photographs are taken by using Hitachi-S-3000H SEM Machine. For this test, a small piece of film of about 3 cm x 1 cm size is fixed on the sample holder using adhesive tape and is then covered with thin layer of sputtered gold to improve image resolution. (The films are prepared from N-Methyl-2-pyrrolidinone (NMP) as a solvent to dissolve the polymer to give the polymer solution. The polymer solution are then casted onto the glass plate and it is allowed to dry at 40 ° C for two hours).

III. Results and discussions

Polyaniline is a phenylene-based polymer having 'NH' group flanked on the either side of the phenyl rings and can exist in different oxidation states (2). The various physico-chemical properties of polyaniline can be said to be due to the presence of 'NH' group. PANi-EB possess two type of sites, amine (-NH-) and imine (-N=) with pKa value of 1.05 and 2.55. Therefore, any dopants whose pKa value falls within that range would be a suitable dopant and those dopants would bring a certain good properties to Polyaniline. In PANi synthesis, the protons available from the dopant determine the conductivity of PANi. In case of the reaction with simple mineral acids like HCl, the imine sites are preferred to coordinate with the H^+ ion over the amine groups. This generates charge carriers and brings metal like conductivity to emeraldine base, which is otherwise, an insulator (Fig.1). The protons are added to -N= sites while the number of electrons in the chain remain constant and so polyaniline is known as a non-redox, protonic polymer. When metal carbonates are dissolved in water, complete ionization of the salt and salvation of the metal cation occurs. It is known that salvation [27] of transition metal by water molecules brings acidic character to the solution due to the equilibrium reaction $\text{M}(\text{H}_2\text{O})_6^{+Z} + \text{H}_2\text{O} \rightarrow \text{M}(\text{H}_2\text{O})_5(\text{OH})^{(Z-1)+} + \text{H}^+$. The strength of the acidity in terms of pKa is determined by the electro negativity of the metal ion. The Ferrous -5- sulphosalicylate complex has pKa1 = 5.05 and pKa2 = 10.7; manganese -5- sulphosalicylate complex has pKa1 = 5.24 and pKa2 = 2.9; cobalt -5- sulphosalicylate complex has pKa1 = 6.13 and pKa2 = 3.69; nickel-5-sulphosalicylate complex has pKa1 = 5.9 and pKa2 = 4 and copper-5-sulphosalicylate complex has pKa1 = 2.7 and pKa2 = 6.7 [28 (a) & (b)] and thus these complexes are mere possessing the satisfactory pKa value of polyaniline for the protonation of two imine nitrogen atoms. The structures of acid complexes are shown in Fig.-2. Hence, 5-Sulpho salicylic acid in the form of metal complexes is used as doping agent by which incorporation of metal ion into polymer sites are achieved.

The various physico-chemical properties change of polyaniline are due to charge transport reaction. Charge transport reaction are strongly influenced by the counter anions and its concentration and nature and it may take place by the interaction among the polymeric chains or between the dopants and polymeric chains. The conductivity and magnetic susceptibility studies are proved the existence of charge transport reactions in polyaniline compounds.

3.1 Conductivity studies

First PANi is doped with different concentration of 5-sulphosalicylic acid and the conductivity is measured by four probe method and the data is used for comparison. Similarly PANi is doped with the above acid complexes. The doping is carried out in three different ways. I) Doping of Polyaniline by metal carbonates. II) Doping of Polyaniline with metal carbonates in the presence of different concentrations of 5- sulphosalicylic acid (5-SSA). III) Doping of polyaniline with different concentration of 5- sulphosalicylic acid (5-SSA). The doped polymers showed the high conductivity like metals and the data for the conductivity are shown in Table-1. When aqueous metal carbonate (Metal= Mn, Fe, Co, Ni, and Cu) is used for doping by stirring for 4 hours, the color of emeraldine base (EB) is remained and un-changed. The final products are blue in color and the conductivity of the samples is increased marginally. The observations are recorded in Table-1. Doping of metal carbonate in the presence of 5-sulpho salicylic acid is found to be effective in the presence of 5-Sulphosalicylic acid. For the systematic study, the concentration of acid is increased and the conductivity is checked at fixed metal concentration (0.1M) and the acid concentration is varied from 0.1 to 0.2M. In all the cases, the conductivity of PANi is increased with increase of acid concentrations. In the case of 5-sulphosalicylic acid (5-SSA) doped PANi, the conductivity is increased from 0.06 (S/cm) to 0.1(S/cm) for 0.1M and 0.2M 5- sulpho salicylic acids respectively. The increase in conductivity is due to increase of the level of protonation of the polymer. Aqueous solutions of 0.1M Manganese carbonate (no color) doped PANi showed the conductivity of 5.0×10^{-6} S/cm. 0.1M 5-Sulpho salicylic acid salt solution of Manganese carbonate doped PANi showed the increase of conductivity of 7.3×10^{-4} S/cm. 0.1M manganese-bis-5-sulpho salicylate diaqua complex doped PANi showed the conductivity of 2.488×10^{-3} S/cm (doping level: 51.4%). The ferrous carbonate doped PANi showed the conductivity of 2.02×10^{-4} S/cm. The complex of 0.1M ferrous 5-sulphosalicylate tetra aqua complex (reddish pink color solution) doped PANi showed the conductivity of 2.67 S/cm and it increased to 3.3 S/cm for

0.1M Fe (5- SSA)₂H₂O complex. It is due to increasing of the acid concentration of the doping solution. Thus conductivity depends on the electronic structure of polyaniline and the stability of charge formation [29, 30, 31, 32]. Moreover, the doping is more effective when the viscosity of the metal complex ion increases. When 0.1mole Cobalt carbonate is taken with 0.1mole 5-SSA, the complex (0.1M) doped polyaniline showed the conductivity of 2.2×10^{-4} S/cm. The complex of 0.1M Cobalt carbonate- 0.2M 5-sulpho salicylic acid doped polyaniline showed the increased conductivity of 0.03 S/cm (doping level: 62.2%). Thus the conductivity depending upon the formation of possible ionic species. 0.1M Nickel carbonate - 0.1 M 5- SSA complex ion doped PANi showed the conductivity of 9.4×10^{-3} S/cm. The mixture solution of 0.1M nickel carbonate and 0.2M 5-SSA showed the conductivity of 16×10^{-3} S/cm to the doped PANi. The aqueous solution consisting of 0.1M Cu(5- SSA)4H₂O doped PANi showed the conductivity of 0.05 S/cm. but the aqueous 0.1M Copper - bis-5- Sulphosalicylato diaqua complex solution (green color) doped PANi showed the increased conductivity (0.28 S/cm). Thus the metal ion complexing with 5-sulpho salicylic acid doped PANi showed the improved conductivity [17]. Table -1 shows the conductivity data of PANi compounds.

3.2. Magnetic susceptibility studies

According to A.J.Epstein and A.G.MacDiarmid, the magnetic susceptibility of conjugated polymer is of two components. 1). Temperature dependent magnetic susceptibility (Curie magnetic susceptibility). It is due to localized spins; 2) Temperature independent magnetic susceptibility (Pauli magnetic susceptibility). It arises from the delocalized spins within the conjugated polymer. In these experiments, transition metal ions doped polyanilines exhibited a positive value of magnetic susceptibility (paramagnetic behaviour), but 5-sulpho salicylic acid doped PANi showed a negative magnetic susceptibility value (diamagnetic behaviour) but they exhibited high conductivity, due to the presence of bipolarons. When 5-sulpho salicylic acid is used as dopant with metal ion and when it's doping level increases, then dc- Magnetic susceptibility value decreased. This may be due to instability of metal ion in acid solution. The magnetic data of the doped PANi is shown in Table – 1. Many others reported the similar results. Tang et al doped PANi with mahemite concluded that magnetization depend on dopants concentration. Elamin et al reported the magnetic susceptibility value of 10^{-4} for the compounds of PANi- HCl, PANi-H₂SO₄ and PANi-tartaric acid [33]. In this experiment, the dc -magnetic susceptibility for pure PANi-EB is found to be $- 0.2931 \times 10^{-6}$ emu/g. But the metal ions like manganese. Ferrous, Cobalt, Nickel or Copper doped PANi showed positive magnetic susceptibility values. The diamagnetic property of 5-sulphosalicylic acid doped PANi is due to dominant diamagnetic character of its constituent elements rather than the formed polarons. The Ferrous and manganese ions doped PANi showed the high magnetic susceptibility values due to more number of unpaired spins available in their electronic structure. Nickel or copper ion doped PANi showed the poor magnetic susceptibility value which can be correlated with their less number of unpaired spin in metal ion system. The dc -magnetic susceptibility value for 0.1M manganese carbonate doped PANi is 2.3245×10^{-6} (g/mole) at room temperature. It is observed that when 5-sulphosalicylic acid is used as ligand for Mn²⁺ and when the complex is used as dopant, the dc -magnetic susceptibility increases with an increase in dopant level. This is due to the increase of paramagnetic impurities within that substances. At 51.4% doping level, the compound showed the decreased dc -magnetic susceptibility value due to intake of dopant acid on the polymeric chain. The dc -magnetic susceptibility value for 0.1M Ferrous carbonate doped PANi is found to be 1.91×10^{-6} (g/mole) and for 0.1M Ferrous -5-sulphosalicylato tetra aqua complex doped PANi, it is to be 4.37×10^{-6} emu/g (doping level:29.6%) respectively. For 0.1M Ferrous-bis- 5-sulphosalicylato diaqua complexes doped PANi, it is found to be 3.32×10^{-6} emu/g (doping level: 36.5%). This decrease in the magnetic susceptibility value is accounted for the diamagnetic character of the acid (5-SSA). 0.1M cobalt carbonate doped PANi showed the magnetic susceptibility value of 1.2838×10^{-6} g/mole, but the magnetic susceptibility value for 0.1M Co(5SSA)4H₂O is found to be 1.79×10^{-6} g/mole. This indicates that 5-SSA is acting as a binding agent for the metal ion to the polymer. 0.1M Co (5SSA)₂ 2H₂O doped PANi complex showed the high magnetic susceptibility value of 2.98×10^{-6} g/mole (doping level: 62.21%). 0.1M Nickel carbonate doped PANi showed the χ_g value of 0.8452×10^{-6} g/mole. The d.c-magnetic susceptibility value for 0.1M Ni (5SSA) 4H₂O doped PANi is found to be 1.123×10^{-6} g/mole (doping level: 26.6%). The χ_g value increased when 0.1M Ni(5SSA)₂ 2 H₂O is used as dopant to PANi ($\chi_g = 2.24 \times 10^{-6}$ g/mole). It is due to increase in doping level of magnetic impurities (doping level: 24.0 %). 0.1 M CuCO₃ doped PANi had the magnetic susceptibility value of 0.2296×10^{-6} g/mole. The dc- magnetic susceptibility for 0.1M Copper – 5- Sulpho salicylato tetra aqua complex ion doped PANi is found to be 1.187×10^{-6} g/mole. This value decreased for 0.1M Cu (5SSA)₂ 2 H₂O complex ion doped PANi ($\chi_g = 0.656 \times 10^{-6}$ g/mole (doping level: 84.5%). This may be due to the instability of metal ion in the acid solution. Thus increase or decrease of χ_g value is due to increase or decrease in the magnetic impurities added to the polymer. The magnetic susceptibility values depend on the preparation conditions of the polymer compound.

3.3.FT-IR studies

IR spectra recorded in the range of 400 – 4000 cm^{-1} (Fig.-3) for the metal ion -5-SSA complex doped PANi. The secondary amine N–H stretching vibration observed at 3400 cm^{-1} . The bands at 1571 and 1483 cm^{-1} are characteristic bands of nitrogen quinoid and benzenoid and are present due to the conducting state of the polymer. These bands show the blue shift from 1571 to 1613 cm^{-1} for the over oxidized PANi. These changes are indicative of the conversion of the benzenoid (B) rings to quinoid (Q) rings in the PANi matrix. The band at 1309 cm^{-1} is assigned to C –N stretching. The asymmetric N-H is stretching vibration at 1250 cm^{-1} . The strong peak at 1152 cm^{-1} is attributed to aromatic delocalization (Polaronic peak of emeraldine salt) or C-H bending vibration of benzenoid or Quinoid rings. The aromatic 1, 4 ring-substituted peaks is observed at 828 cm^{-1} (2). The out of plane bending vibration is exhibited in between 600 – 700 cm^{-1} . The peak at 570 cm^{-1} is attributed to metal ion binds with the polymer. The IR – spectral data for the doped PANi is presented in the Table – 2.

3.4 XRD studies

Fig.-4 shows the XRD powder patterns of Polyanilines doped with metal complexes. The peaks at $2\theta = 8, 12, 20,$ and 24° are attributed to the distance of adjacent polymer aromatic rings. It is said that the peak at $2\theta = 20^\circ$ is due to crystalline nature of pernigraniline polymer [36]. The peaks at $2\theta = 8, 12^\circ$ are indicating the closeness of aromatic rings of doped polyaniline [23, 34]. The disappearance of peak at $2\theta = 12^\circ$ indicating the diffusion of dopant in the polymeric chain. The XRD peak at $2\theta = 72.9^\circ$ may be the formation of new phases possibly formed due to the composite formation with cobalt-5-sulpho salicylate. The small peaks at 52, 72 and 88° are new phases for the metal complex ion doped PANi.

3.5 SEM studies

SEM studies are carried out for PANi-EB and the doped PANi salt of metal complexes. In Fig.5 (k), PANi -EB shows a uniform homogenous structure. Similar structure is reported by M.K. Ram et al [36]. The addition of dopant results the formation of large grains particles. It is reported that solid consists of large grain boundaries are strongly influence the mechanical and electrical properties. The film of 0.1M manganese-5-sulphosalicylate doped PANi is used to prepare a film from NMP solvent. It shows the small grains and the larger aggregates with globular structure due to aggregation of particles. The aggregate size is varied from 50-500 μm as can be seen from Fig. 5(b). The SEM picture of Ferrous -5- sulphosalicylate doped PANi film showed the small elliptical shaped crystallites of larger than 100 μm [Fig.(5d)]. The small grains are as a result of the agglomeration of polymer molecules. The SEM picture of cobalt-5-sulphosalicylate doped PANi showed the large agglomerated particles of various shapes around 50 – 400 μm [Fig.5(f)]. SEM studies on the film cast of nickel- 5-sulphosalicylate doped PANi is found to be uniform with microcrystallinity. The larger aggregate may be the result of polymer- dopant- solvent interactions. It has many pores as can be seen from Fig.5(h). The larger aggregates give better crystallinity to films. The SEM picture of copper- 5- sulphosalicylate doped PANi showed the granular structure with the grain size of 5 μm [Fig.5(j)]. It shows copper particles get embedded in the PANi surface. The SEM pictures of metal carbonate doped Polyaniline are given for comparison with the SEM pictures of metal carbonate of 5- sulphosalicylic acid complex doped Polyaniline. The manganese carbonate doped PANi shows the uniform smooth surface [Fig.5 (a)]. Similarly the SEM pictures of other metal carbonates doped Polyaniline showed the crystallites of various shapes. The sizes are varied from 10 – 50 μm .

Estimation of metal -5-sulphosalicylate doped PANi

The amount of metal ions (Mn, Fe, Co, Ni and Cu) in the doped polyaniline is estimated by boiling the metal –5-Sulphosalicylatedoped PANi (where Metal=Mn, Fe, Co, Ni and Cu) in con. Nitric acid to destroy the polymer. The completion of the reaction is indicated by the disappearance of color. The remaining colorless sample is its metal oxides. Atomic absorption spectroscopic (AAS) method is used to find the amount of metal ion incorporated in PANi matrix. It is estimated to be around 0.23-1.22% and the results are shown in Table-3.

IV. Conclusions

The preparation of high spin organic compound is considered because of its scientific interest. High spin organic compound which gets attraction towards a magnet at room temperature is recent research development. In this study, transition metal ions such as $\text{Mn}^{+2}, \text{Fe}^{+2}, \text{Co}^{+2}, \text{Ni}^{+2}$ and Cu^{+2} were used to dope PANi. The so prepared PANi compounds were characterized by FT-IR spectra and X –ray diffraction studies. The magnetic susceptibility and conductivity values of the transition metal ion doped polyanilines were discussed. The following conclusions were drawn from our studies. In Conductivity studies, the protonation makes PANi as a highly stable conductive material. The DC-conductivity of the conducting polyaniline is found to be in the range of $10^{-6} - 0.1 \text{ S/cm}$. The electron delocalization over the polymeric chain creates polarons which are responsible for electronic conductivity. In FT-IR spectral studies, an almost identical spectrum is observed to that of usual PANi. The absorption band at 1140 cm^{-1} in the doped PANi system is the characteristic band and is due to charge delocalization on the polymer. In the undoped polymer, the intensity of this band

becomes very weak. The XRD study showed that polyaniline is amorphous in nature with a broad peak appears in between $2\theta = 8 - 25$. The more protonated PANi showed a broad peak around at $2\theta = 25$. In SEM studies, the SEM picture of the polymer shows the inhomogeneous, non-uniform globular structure. The uniform globular structure of doped PANi showed good conductivity for the compound. In Magnetic susceptibility studies, 5-Sulpho salicylic acid (5-SSA) doped PANi and PANi- EB showed a negative magnetic susceptibility indicating that the compounds are diamagnetic in nature. It is due to the dominant diamagnetic value of its constituent elements than the formed polaronic value. On the other hand, paramagnetism has been observed for all the metal ions doped PANi. The metal ion such as Manganese, Ferrous, Cobalt, Nickel and Copper when separately used as dopant to PANi, showed the positive magnetic susceptibility values. The Ferrous and manganese ions doped PANi showed large positive magnetic susceptibility values due to more number of unpaired electron in their metal ion system. The nickel and copper ion doped PANi showed poor magnetic susceptibility values which can be correlated with their less number of unpaired electron in their metal ion spin system.

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References

- [1]. American Chemical society, International Symposium on Inorganic and metal-containing Polymeric Materials held on September 11- 14, 1989, in Miami Beach, Florida edited by Plenum Press, 1990, Network.
- [2]. D.C-Trivedi, Hand book of Organic Conductive Molecules and polymers edited by H .S. Nalwa, John Wiley & Sons Ltd.,1997, Vol.2, p.505- 572.
- [3]. Dinesh Chandra Trivedi and Sundeep Kumar Dhawan in Frontiers of Polymer
- [4]. Research, edited by P.N Prasad and I.K. Nigam, Plenum press, Newyork, 1991.
- [5]. D.C- Trivedi, J.Solid State Electrochem. (1998) 2: 85-87
- [6]. Conducting polymers, Fundamental & applications, ed.by Prasanna Chandra Sekhar.1999Lower academic publication
- [7]. JayashreeAnand, S.Palaniappan, and D.N. Sathyanarayana, J.Phys.Chem.1995, 99,10324 – 10328.
- [8]. Lijuan Zhang, and Meixiang Wan, J.Phys. Chem. 2003,107, 6748 - 6753.
- [9]. MarystelaFerreira, Fritz Huguenin, ValtencirZucolotto, Jose Eduardo Pereira da Silva, Susana I. Cordopa de Torresi, Marcia L. A. Temperini, Roberto M. Torresi and Osvaldo N.Oliveira Jr. J.Phys. Chem., 2003,107, 8351 – 8354.
- [10]. Michael Gill, John Mykytiuk, Steven P. Armes, John L. Edwards, Terry Yeats, PeterJ.Moreland and Christ Mollet, J.Chem.Soc, Chem. Commun., 1992,108 - 109.
- [11]. Rabin Bissessur, Donald C. DeGroot, Jon L.Schindler, CarlR.Kannewurf, and Mercouri G. Kanatzidis, J.Chem.Soc. Chem. Commun., 1993,687.
- [12]. ShengjunTian, Jianyun Liu, Tao Zhu and Wolfgang Knoll, J.Chem.Soc. Chem.Commun.2738 – 2739, 2003.
- [13]. Nobuyuki Koura, HirokazuEjiri, and Kazuyuki Takeishi, J.Electrochem.Soc. 1993,140, 602 – 605.
- [14]. Frank Rourke and Joe A.Crayston, J.Chem.Soc, Faraday Trans; 1993, 89(2), 295 –302.
- [15]. M.I. Boyer, S.Quillard, G.Louarn, G. Froyer, and S. Lefrant, J.Phys. Chem. 2000,104, 8952 – 8961.
- [16]. 15.V.Tsakova,D.Borrisov,B.Ranguelov,Ch. Stromberg,J.W.Schultze,Electro chimicaActa46(2001)4213 - 4222.
- [17]. R.Murugesan, E. Subramanian, Bull. Mater.Sci., 26(5)2003, p.529 – 535, IndianAcademy of Sciences.
- [18]. Meixiang Wan, Weixia Zhou, JunchaoLi., Synthetic Metals 78 (1996) 27 –31.
- [19]. B.Z. Tang, Y.H. Gang, Q.H.Sen, X.X.Zhang et al., Pure. Appl. Chem.72 (2000) 157.
- [20]. Park-JE, Park –SG, Koukitu – A, Hatozaki-O, Oyama – N, Synthetic metals 2004, Vol.141, p. 265 – 269.
- [21]. Hasik-M, Paluszkiwicz- C, Wenda –E, Vibrational spectroscopy, 2002, Vol.29, Iss. 1-2,p. 191 – 195.
- [22]. Wei-JH, Guan –JG, Chen –WY, Yuan –RZ, ActaPhysico – ChimicaSinica 2002 ,Vol.18, p. 653 – 656.
- [23]. Drelinkiewicz - A,Hasik – M,Kloc –M, Synthetic Metals 1999, Vol. 102, p. 1307 –1308.
- [24]. Gurunathan –K, Trivedi – DC, Materials letters 2000, Vol. 45, Iss. 5, p. 262 – 268.
- [25]. Sobczak –JW, Kosinski –A, Jablonski-A, Palczewska-W, Topics in Catalysis2000, Vol. 11, Iss. 1 – 4, p.307 316.
- [26]. A.V.Saprigin, K.R.Brenneman, W.P.Lee, S.M.Long, R.S.Kohhlman, Synthetic Metals100 (1999) 55 – 59
- [27]. P.V.Khadikar, S.M.Ali, B.Heda, Journal of thermal analysis, Vol.30 (1985) 305 – 317.
- [28]. Gary Wulfborg, Inorganic Chemistry, Viva Books pvt Ltd and University Sciencebooks, USA, First edition, 2002, p.59.a) Stability constant of metal ion complexes- compiled by L.G.Sillen and A.E.Martell, 1964, The Chemical Society, London, p.548 b) Critical stability constants, other organic ligands, edited by Arthur E. Martell andRobert M. Smith, Vol.3, 1977, Plenum press, Newyork, p. 190 - 191
- [29]. Zennvijlle, Frans, Brunisholz, Georges; Inorg.Chim.Acta 1985,102 (2), 205 –10 (Eng.).
- [30]. A.Zykwinska, W.Domagala, B.Pilawa, M.Lapkowski, Electrochimica.Acta 50 (2005)P.1625 –1633.
- [31]. 31. Ralph H.Young, John J. Fitzgerald, J.Phys.Chem.1995, 99, p.4230 – 4240.
- [32]. 32. Kiyoshi Kanamura,YasunoriKawai, SusumuYonezawa and Zen –ichiroTakehara,J.Phys.chem. 1994, 98,p.13011 – 13016.
- [33]. 33. ElaminAbdulkader. M; Yao, Kailun.Jpn.J.Apply.Phys.part 1, 1999, 38(8), 4809 –4811.
- [34]. 34. M.Vijayan, D.C- Trivedi, Synthetic metals 107 (1999) p. 57 – 64.
- [35]. 35. K.G. Neoh, E.T.Kang, and K.L. Tan, J. Phys Chem.1992, 96, p.6777 –6783.
- [36]. 36. M.K.Ram, N.S. Sundaresan, and B.D.Malhotra, J.Phys.Chem .1993, 97, 11580 –11582.

Table – 1: Conductivity (S/cm) and Magnetic susceptibility data of metal ions doped PANi and Polyaniline– EB

Complexes	Conductivity (S/cm)	Doping percentage	dc - magnetic susceptibility (χ_d) g/mole
Polyaniline(PANi) in Emeraldine base form	Insulator	0	-0.2931×10^{-6}
0.1M 5-SSA doped PANi	0.06	31.4	-0.256×10^{-6}
0.2M 5-SSA doped PANi	0.08	37.64	
0.3M 5-SSA doped PANi	0.3	39.2	
0.1M MnCO ₃ doped PANi	5×10^{-6}	6	2.32×10^{-6}
0.1M Mn(5SSA) 4H ₂ O doped PANi	7.3×10^{-4}	26.3	2.39×10^{-6}
0.1M Mn (5SSA) ₂ 2 H ₂ O doped PANi	2.488×10^{-3}	51.4	1.595×10^{-6}
0.1M FeCO ₃ doped PANi	2.02×10^{-4}	6.5	1.91×10^{-3}
0.1M Fe (5SSA) 4H ₂ O doped PANi	2.67	29.6	4.37×10^{-6}
0.1M Fe (5SSA) ₂ 2 H ₂ O doped PANi	3.3	36.5	3.32×10^{-6}
0.1M CoCO ₃ doped PANi	1.34×10^{-5}	~ 10	1.2838×10^{-6}
0.1M Co(5-SSA) 4H ₂ O doped PANi	2.2×10^{-4}	31.4	1.79×10^{-6}
0.1M Co(5SSA) ₂ 2 H ₂ O doped PANi i	0.03	62.21	2.98×10^{-6}
0.1M NiCO ₃ doped PANi	~ 10^{-3}	5.4	0.8452×10^{-6}
0.1M Ni (5SSA) 4H ₂ O doped PANi	9.4×10^{-3}	26	1.123×10^{-6}
0.1M Ni(5SSA) ₂ 2 H ₂ O doped PANi	10×10^{-3}	51	2.24×10^{-6}
0.1M CuCO ₃ doped PANi	3.378×10^{-3}	10	0.2296×10^{-6}
0.1M Cu(5SSA) 4H ₂ O doped PANi	0.28	38	1.187×10^{-6}
0.1M Cu(5SSA) ₂ 2 H ₂ O doped PANi	0.05	84.5	0.656×10^{-6}

Table – 2: FT-IR data of metal ions doped PANi and % of metal ions in doped PANi

S.No.	Polymer sample	IR absorption Bands (cm ⁻¹)	% of metal
1	0.1M Mn(5SSA) 4H ₂ O doped PANi	1600,1560,1490,1307,1150, 1030, 827	0.23
2	0.1M Fe (5SSA) 4H ₂ O doped PANi	1655,1578,1499, 1400,1309, 1152,1030, 828	1.3
3	0.1M Co(5SSA) 4H ₂ O doped PANi	1577,1491, 1303,1142,828	1.1175
4	0.1M Ni(5SSA) 4H ₂ O doped PANi	1583,1494,1377,1302, 1143,828	0.67
5	0.1M Cu(5SSA) 4H ₂ O doped PANi	1744,1572,1502, 1298, 1109, 820	0.85

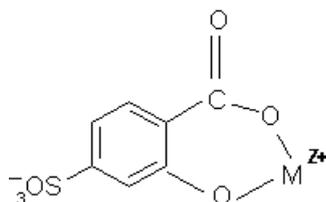


Fig 1- General structures of M^{Z+} complex of 5-Sulphosalicylate where M^{Z+} = Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺ and Cu²⁺

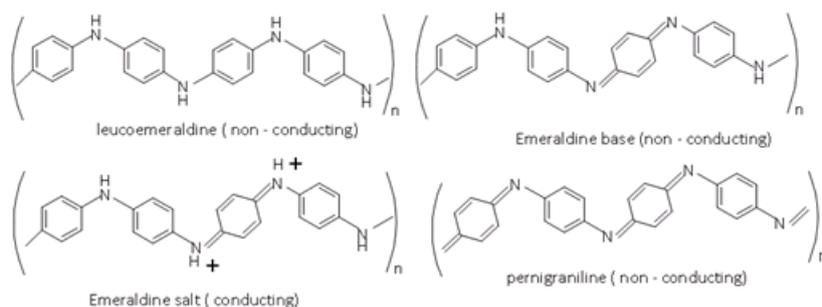


Fig.2-. Various forms of Polyanilines

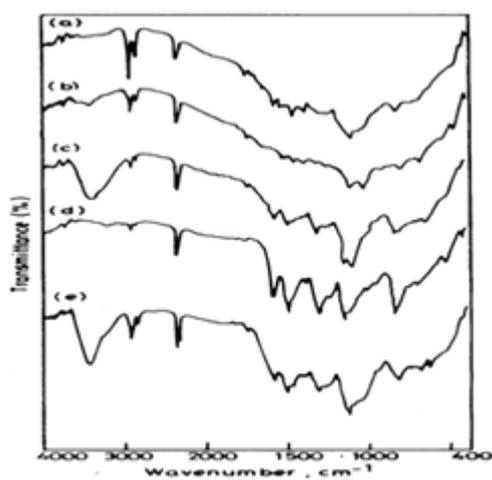


Fig.3. FT-IR spectra of
a) 0.1M Mn(5SSA) 4H₂O doped PANi; b) 0.1M Fe (5SSA) 4H₂O doped PANi;
c) 0.1M Co(5-SSA) 4H₂O doped PANi ;d) 0.1M Ni(5SSA) 4H₂O doped PANi
e) 0.1M Cu(5SSA) 4H₂O doped PANi;

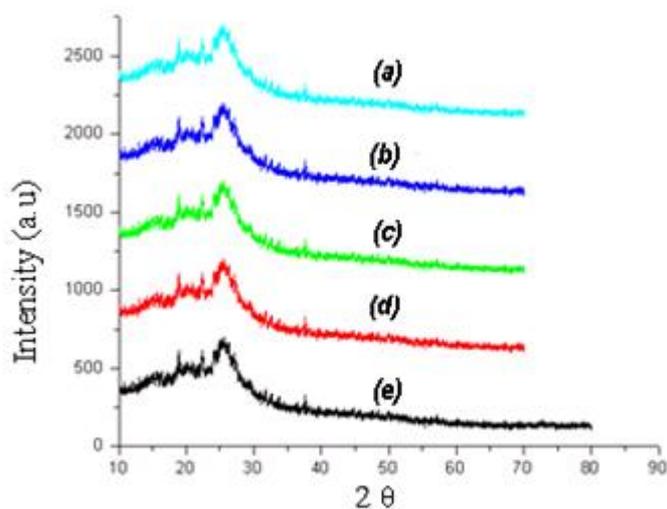


Fig.4.XRD powder patterns of
a) 0.1M Mn(5SSA) 4H₂O doped PANi; b) 0.1M Fe (5SSA) 4H₂O doped PANi;
c) 0.1M Co(5-SSA) 4H₂O doped PANi ;d) 0.1M Ni(5SSA) 4H₂O doped PANi
e) 0.1M Cu(5SSA) 4H₂O doped PANi;

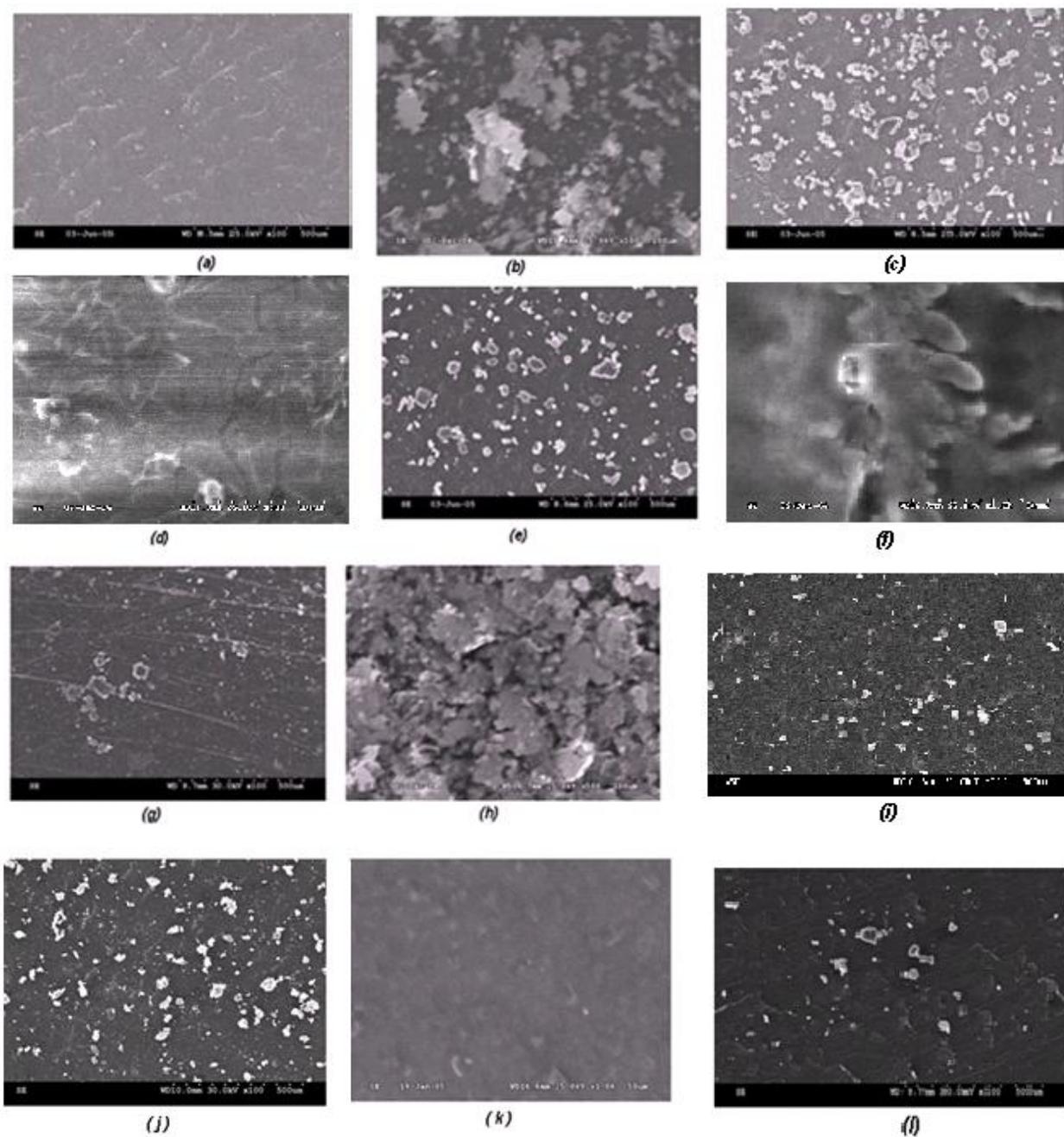


Fig.5- SEM micrographs for
 a) 0.1M $MnSO_4$ - PAni; b)0.1M Mn(5SSA) $4H_2O$ doped PAni;
 c) 0.1M $(NH_4)_3 Fe (SO_4)_3$ - PAni ; d) 0.1M Fe(5SSA) $4H_2O$ doped PAni;
 e) 0.1M $CoSO_4$ - PAni; f) 0.1M Co(5SSA) $4H_2O$ doped PAni;
 g) 0.1M $NiSO_4$ - PAni; h) 0.1M Ni(5SSA) $4H_2O$ doped PAni;
 i) 0.1M $CuSO_4$ - PAni ; j) 0.1M Cu(5SSA) $4H_2O$ doped PAni;
 k) emeraldine base films; (l) 5-SSA -PAni