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Infrared Spectra: Useful Technique to Identify the Conductivity Level of Emeraldine form of Polyaniline and Indication of Conductivity Measurement either Two or Four Probe Technique

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Abstract

A new insight was watched the connection between's the conductivity and Fourier Transform Infrared (FT-IR) spectra of the emeraldine type of polyaniline (PANI) structures. The conductivity of polyaniline emeraldine salt (PANI-ES) can be varied from 10^{1} to 10^{-12} S cm^{-1}. FT-IR spectrum is a tool to determine the conductivity level and also conductivity measuring methods of PANI system, i.e., either two probe or four probe techniques. This information is very useful for the researcher and industrialists working on emeraldine form of PANI systems to identify the conductivity level and method of measurements from FT-IR spectra. This data was seen from the infrared spectra of different PANI salts obtained by the oxidation of aniline in water/solvent medium by ammonium persulfate (APS) without utilizing any acids. PANI-ES samples having reasonably good conductivity (> 0.3 S cm^{-1}) showed mostly nanowires or nanorods morphology, whereas, lower conductivity (<0.3 S cm^{-1}) samples showed mostly agglomerated spheres or particles morphology. In these investigations, however, no report was made of the use of infrared technic to determine the conductivity of PANI system.

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Introduction

Polyaniline is most studied conducting polymer throughout the world because of its easy synthesis, environmental stability, reasonably good electrical conductivity, tunable electrical properties via oxidation/reduction chemistry (unique acid/base doping/dedoping process), and inexpensive material. PANI exists in three different forms, i.e., leucoemeraldine (completely insulator), emeraldine (insulator to the semiconductor) and

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pernigraniline (conductive). Polyaniline can be synthesized by chemical oxidative synthesis,[1] electrochemical polymerization,[2] rapid mixing polymerization,[3] Emulsion Polymerization,[4] in situ seeding polymerization[5] or using templates and surfactants.[6] Among these techniques, interfacial polymerization is a standout amongst the best methodologies, which creates amazing PANI nanostructures in extensive quantities.[7] The conductivity of polyaniline emeraldine base (PANI-EB) increments reversibly with doping from the un-doped base (10^{-10} S cm^{-1}) to the completely doped, emeraldine directing salt frame (10^{1} S cm^{-1}). The doping level can be tuned basically by controlling the pH of the dopant and this can be controlled either chemically or electrochemically by changing the oxidation state. The tunable electrical conductivity accomplished by doping/de-doping makes PANI is a promising material for some, applications incorporating into batteries, sensors, actuators, electromagnetic protecting, antistatic coatings, corrosion resistance, electro-optic, electrochromic gadgets, and division layers and so on. Synthesis, properties, and uses of emeraldine type of PANI frameworks have been accounted in the reviews.[8-10]

PANI is typically prepared in water medium at room temperature[11] or at low temperature.[12,13] The response continues to the development of a green encourage. PANI can likewise be set up in the solid state when no dissolvable is used,[14,15] for the two strategies just granular morphology is typically framed. Then again, if polymerization continues at the interface of two immiscible fluids, PANI nanofibres are obtained.[16,17] On the off chance that amid oxidation a surfactant or a water-solvent polymer is added to the reaction, PANI colloids are shaped.

It has been exhibited by Gospodinova et al[18] that the polymerization of aniline additionally continues well in water, with no additional acid, when ammonium peroxydisulfate was utilized as an oxidant. In our gathering likewise already revealed that the aniline was oxidized with APS at high temperature with no acid dopant.[19]

In the present work, PANI-ES were set up without utilizing any additional hazardous acid by the oxidation of aniline utilizing APS. PANI-ES was de-doped to PANI-EB utilizing aq. NaOH. In the present paper, aniline was oxidized with ammonium peroxydisulfate in water/organic solvent medium without any additional acid, and was evaluated by morphology, FT-IR and conductivity measurements. The conductivity of the sample >0.1 S cm^{-1} to be estimated by means of four probe technique, and the conductivity $<10^{-9}$ S cm^{-1} to be estimated utilizing high resistance meter. Conductivity in the range 10^{-2} to 10^{-9} S cm^{-1} can be estimated utilizing even a typical multimeter. Four probe procedures include the estimation of voltage by passing the current. Subsequently, it needs consistent current source and voltage estimation hardware with the required exactness, which are costlier gear for the business. This paper reports that FT-IR could be utilized to discover the conductivity level in emeraldine frameworks, and the strategy for estimation of the conductivity of the emeraldine samples through high resistance meter, two or four probe methods.

Polyaniline-sulfate salt (PANI-H_2SO_4)[20] was prepared by traditional polymerization pathway by the oxidation of aniline within the sight of sulphuric acid utilizing ammonium persulfate oxidant (APS).

Materials and Methods

Materials

Aniline (AR grade) was obtained from S. D. Fine Chemicals, Mumbai, India was vacuum distilled prior to use. Ammonium persulfate and Sulphuric acid (H_2SO_4) were obtained from Sigma Aldrich,Bengaluru, India. All the solvents (AR grade) were obtained from Rankem, Hyderabad, India. All the reactions were carried out with distilled water. Polyaniline-sulfuric acid (PANI-H_2SO_4) salt and its corresponding base were prepared by following our earlier report.[20]

Characterization

The details of characterization techniques are given in Table 1.

Experimental Procedure

Synthesis of PANI-ES in organic solvents without using acid dopants

A progression of polyaniline emeraldine salts (PANI-ES) incorporated with the nonappearance of corrosive through interfacial polymerization[4] of

Table 1: Techniques used along with information and their equipment details

Technique	Condition	Equipment details
Fourier-transform infrared spectroscopy (FT-IR)	Sample was evenly dispersed in Potassium bromide (KBr) by grinding and pressed into pellet	Model 670, Nicolet Nexus, (Minnesota, USA)
Scanning electron microscopy (SEM)	Powder samples	Hitachi S-4300 SE/N FE-SEM, (Hitachi, Tokyo, Japan)
Two-probe conductivity measurement	Pellet (13 mm diameter and 1.5 mm thickness)	Keithley, Cleveland, OH, model-2010
Four-probe conductivity measurements	Pellet (13 mm diameter and 1.5 mm thickness)	Keithley, Cleveland, Ohio, Current source-6220 and nanovoltmeter -2182A

aniline in water and natural dissolvable blend. In an ordinary test, 15 mL of solvent was taken in a 100 mL tapered flagon and included 1 mL of aniline. An oxidizing specialist APS (2.8 g) in 30 mL of water was added gradually through the side of the funnel shaped flagon amid a time of 15 to 20 min. The response blend was kept at 5 °C in an ice box without mixing for 24h. The green shaded powder was separated, comprehensively flushed with water refined lastly with 250 mL of $(CH_3)_2CO$. The powder test dried at 60 °C till a steady weight.

In this combination of PANI-ES utilizing two arrangements of solvents, i.e., First arrangement of solvents comprising of non-polar solvents, i.e., xylene, toluene, benzene, hexane, dichloromethane (DCM), chloroform and the second arrangement of solvents are polar solvents, i.e., water, methanol, ethanol, isopropyl alcohol (IPA), tetrahydrofuran (THF).

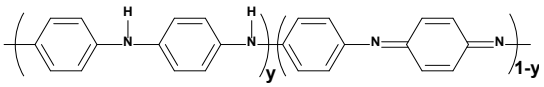
Preparation of PANI-EB

De-doped the polyanilineemeraldine salt (PANI-ES) to polyaniline emeraldine base (PANI-EB) by blending 0.5 grams of PANI-ES in 50 mL of an aq.1 M NaOH for 4 h at enveloping temperature. The blend was isolated and washed with 50 mL of aq.1 M NaOH, 500 mL of deionized water, in conclusion, 50 mL of $(CH_3)_2CO$. The powder was dried at 60 °C until to obtain a constant weight.

Results and Discussions

Morphologies of the PANI-ES prepared in the mixture of aqueous/organic solvents medium are shown in Fig.1. The images showed mostly two types of morphologies, i.e. nanowires or nanorods and agglomerated spheres or particles.

FTIR spectra and conductivity measurements were carried out for the PANI-ES and their corresponding bases. The PANI-EB can, in principle, be described by the following general structure (Structure 1).



Structure 1: General structure of PANI-EB

In the summed up base frame, (1-y) measures the capacity of oxidized units. At the point when (1-y) = 0, polymer has no such oxidized gathering and is ordinarily known as a leucoemaraldine base. The completely oxidized frame, (1-y) =1 is alluded to as a pernigraniline base. The half-oxidized polymer where the quantity of reduced units and the oxidized

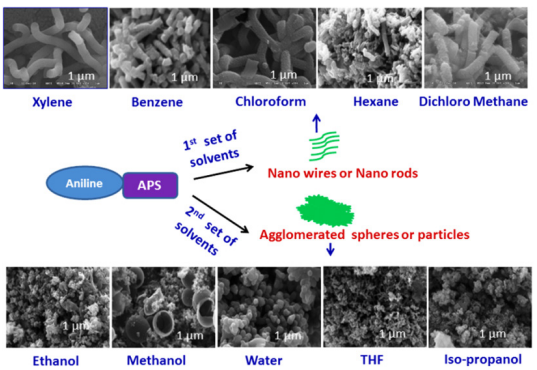
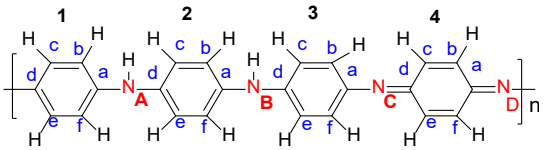
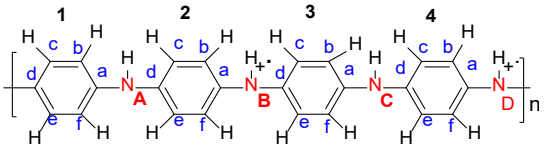


Fig. 1: SEM images of PANI-ES prepared with 1st set of solvents and 2nd set of solvents.

units are equivalent, i.e. (1-y) = 0.5, is of exceptional significance and is named the emeraldine oxidation state or the emeraldine base. The estimation of 'y' changes from 0 to 1 at the same time, the level of carbon; hydrogen and nitrogen percentage is nearly the same. Contemplating the above focuses, the accompanying structures for emeraldine base and emeraldine salt are considered for the present talk (Structures 2 and 3).



Structure 2: Representative structure of PANI-EB.



Structure 3: Representative structure of PANI-ES.

Major peaks are analyzed by considering the above structure of PANI-ES and PANI-EB. PANI-EB has FT-IR functional groups such as N-H, C=C, C≡C, C-C, C-N-C, C≡C-H, C-N=C, 1,4-disubstituted benzene (N_C-C_6H_4-N_D). Peaks due to these functional groups are obtained in the FT-IR spectrum of PANI-EB is shown in Table 2.

On protonation, PANI-EB changes to PANI-ES, wherein, nitrogen atom changes to protonated radical cation ($NH^{+\bullet}$). This PANI-ES has the functional groups such as N-H,N-$H^{+\bullet}$,C=C,C≡C, C-N-C, C≡C-H, C-$NH^{+\bullet}$-C, 1,4-disubstituted benzene (N_C-C_6H_4-$N_DH^{+\bullet}$). Thus in the case of PANI-ES, an extra peak should appear for N-$H^{+\bullet}$(3225 cm^{-1}), and the peak due to C-C (1380 cm^{-1}) disappear when compared with that of PANI-EB. Also, peak shifts are expected due to the aromatic nature of PANI-ES. These changes are also observed in the PANI-H_2SO_4 salt (Table 2). In addition, based on the present result and experience of the authors,the range of the peaks for most of the PANI-salts and bases were identified. These values are also included in Table 2. FT-IR spectra of PANI-H_2SO_4 salt and its base are shown in Fig.2 and the major peaks observed are indicated in Fig. 2.

The FT-IR spectral results for the PANI-ES prepared using various solvents are detailed in Table 3. These PANI-ES spectra showed peaks due to N-H, N-$H^{+\bullet}$, C=C, C≡C, C-N-C, C≡C-H, C-$NH^{+\bullet}$-C,

Table 2: Infrared spectral data of PANI-H_2SO_4 salt and its corresponding base along with the reported PANI salts and their bases

System	N_A-H^d	N_B-$H^{+\bullet}$	C=C 4b-4c	C≡C 1b-1c	C-C str. 4c-4d	C-N-C 1a-N_A-2d	C ≡C-H 4b-H	C-N $H^{+\bullet}$-C 3a-N_D-4d	N_C-C_6H_4-N_D $H^{+\bullet}$. di sub.
PANI-H_2SO_4[a]	3440	3225	1563	1482	NIL	1300	1240	1105	801
PANI base[a]	3380	NIL	1585	1494	1380	1307	1213	1160	828
Reported PANI Salts[b]	3440	3225	1560-1570	1470-1484	NIL	1298-1306	1230-1243	1105-1130	797-803
Reported PANI Bases[c]	3440	NIL	1585-1590	1492-1500	1377-1383	1310-1313	1213-1217	1159-1162	824-835

[a]PANI-H_2SO_4 salt and its base prepared from our earlier report[20], [b] Ref No.[21-24], [c] Ref No.[19,21,25], [d] Very broad peak

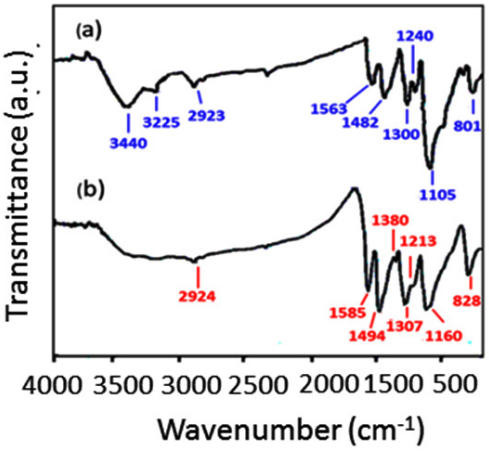


Fig. 2: Infrared spectra of (a) PANI-H_2SO_4 salt and (b) its corresponding PANI base.

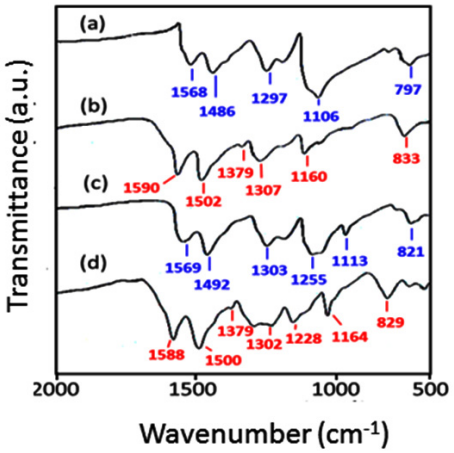


Fig. 3: Infrared spectra of (a) PANI-ES prepared using benzene solvent, (b) its corresponding base; (c) PANI-ES prepared using ethanol solvent, and (d) its corresponding base.

1,4-disubstituted benzene, this signs indicate the formation of PANI in salt form.

FT-IR spectral results for the PANI-EB prepared from various PANI-ES synthesized using various solvents are detailed in Table 4.

Most of the FT-IR peaks of PANI-EB are shifted compared to the PANI-ES peaks due to the formation of aniliniumradical cation (N-H$^{+\bullet}$) in PANI-ES. As representative systems, FT-IR spectra of PANI-ES prepared using benzene (1st set of solvent) and ethanol (2nd set of solvents) and their corresponding bases in the range 2000-500 cm^{-1} are shown in Fig.3 along with their major peak positions.

Two sets of results observed based on the solvents used. The first set of solvents consisting of xylene,

Table 3: Infrared spectral data for PANI-ES salts prepared using 1st and 2nd set of solvents

Emeraldine Salts	C=C 4b-4c	C⁗C 1b-1c	C-C str. 4c-4d	C-N-C 1a-N_A-2d	C⁗C-H 4b-H	C-$NH^{+\bullet}$-C 3a-N_D-4d	N_C-C_6H_4-$N_DH^{+\bullet}$. di sub.	Conductivity (S cm^{-1})
1st Set of solvents								
Xylene	1565	1481	s	1300	1244	1105	799	1.5
Toluene	1567	1484	NIL	1301	1242	1108	799	0.8
Benzene	1567	1486	NIL	1296	1244	1106	797	0.3
Hexane	1567	1484	NIL	1298	1245	1107	799	0.9
DCM	1563	1480	NIL	1300	1241	1104	797	0.3
Chloroform	1560	1482	NIL	1300	1242	1105	799	0.4
2nd Set of solvents								
Water	1574	1497	vs	1306	1260	1147[a]	823	0.009
Methanol	1584	1498	vs	1301	1260	1145[a]	822	0.02
Ethanol	1569	1492	vs	1303	1255	1113[a]	821	0.02
IPA	1569	1499	vs	1293	1260	1116[a]	823	0.0007
THF	1579	1493	vs	1302	1260	1112[a]	820	0.0007

vs – Very small peak observed, s is small [a] peak appears as doublet peak

Table 4: Infrared spectral data for PANI-EB

Emeraldine base	C=C 4b-4c	C⁼⁼C 1b-1c	C-C str 4c-4d	C-N-C 1a-N_A-2d	C⁼⁼C-H 4b-H	C-$NH^{+\bullet}$-C 3a-N_D-4d	N_C-C_6H_4-$N_DH^{+\bullet}$. di sub.
1st Set of solvents							
Xylene	1589	1502	1378	1309	1228	1164	830
Toluene	1590	1502	1379	1314	1229	1162	829
Benzene	1590	1502	1380	1307	1228	1161	833
Hexane	1590	1502	1380	1312	1228	1164	832
DCM	1588	1502	1380	1311	1228	1163	828
Chloroform	1587	1502	1379	1312	1229	1164	830
2nd Set of solvents							
Water	1591	1504	1378	1310	1229	1166	834
Methanol	1589	1488	1379	1310	1228	1160	830
Ethanol	1588	1500	1379	1302	1228	1164	829
IPA	1585	1496	1379	1294	1228	1165	834
THF	1590	1502	1380	1304	1228	1166	830

toluene, benzene, hexane, dichloromethane, chloroform and the second set of solvents are water, methanol, ethanol, isopropanol, tetrahydrofuran. The peaks observed at lower wavenumber for the PANI-ES prepared using the first set of solvents compared to that of the PANI-ES prepared using the second set of solvents. In addition, a peak appears in the case of the second set of solvents at around 1040 cm^{-1} and this peak is due to C-O-C. The clear peak shifts are observed in C=C (quinonoid ring), C⁼⁼C (benzenoid ring),C-$NH^{+\bullet}$-C and N_C-C_6H_4-$N_DH^{+\bullet}$. di substituted benzene. The range of FT-IR peaks observed for reported PANI-salts, PANI-ES prepared using various solvents and its corresponding bases are listed in Table 5.

This Table 5 also indicates the correlation between FT-IR spectrums of PANI systems with its conductivity and method of measurement of conductivity of PANI systems.This information is a very useful researcher and industrialists working on PANI systems to find the conductivity level and method of measurements from FT-IR spectrum.Similarly, theconductivity of PANI-ES shows two sets of value (Fig.4), i.e., >0.3 S cm^{-1} for the first set of solvents and <0.3 S cm^{-1} for the second set of solvents.

Table 5: Correlation between FT-IR peaks with conductivity and its measurement technique

System	C=C 4b-4c	C⁼⁼C 1b-1c	C-$NH^{+\bullet}$-C 3a-N_D-4d	N_C-C_6H_4-$N_DH^{+\bullet}$. di sub.	Conductivity (S cm^{-1})	Resistance Measurement
Reported PANI salts [a]	1560-1570	1470-1484	1105-1130	797-803	3 to 5	Four probe
PANI-ES (1st set of solvents)[b]	1560-1567	1481-1486	1105-1108	797-799	0.3 to 1.5	Four probe
PANI-ES (2nd set of solvents)[b]	1569-1584	1492-1499	1112-1145	820-823	0.02 to 0.0007	Two probe
Bases from PANI salts prepared in various Solvents [b]	1585-1590	1496-1504	1160-1165	828-834	< 10^{-10}	High resistance Meter

[a] Ref No. [21-24], [b] Prepared in this work

A clear correlation observed between the conductivity and FT-IR peak positions for emeraldine salt and its base. Reported emeraldinepolyanilinesalts having conductivity (2 to 5 S cm^{-1}) showed peaks due to C=C, C⁼⁼C, C-$NH^{+\bullet}$-C and N_C-C_6H_4-$N_DH^{+\bullet}$.at lower wavenumbers compared to its corresponding base, which is having very low conductivity (<10^{-10} S cm^{-1}). PANI-ES prepared using first set of solvents are showing conductivity >0.3 S cm^{-1}, which showed FT-IR peaks close to that of PANI-H_2SO_4 salt peaks.

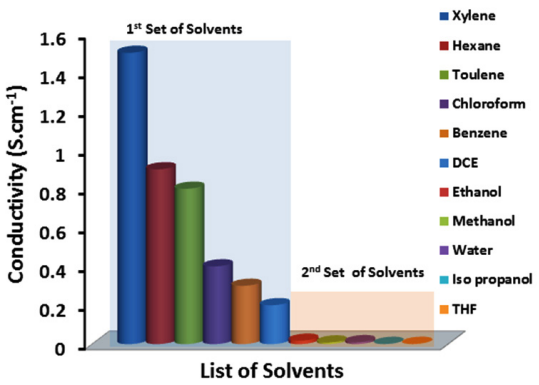


Fig. 4: List of solvents vs. conductivity of PANI-ES salts.

The second set of solvents PANI-ES showed conductivity in the semiconductor region, which showed peaks in between the emeraldine salt and its base. In a similar manner, PANI-ES prepared using first set of solvents with conductivity (>0.3 S cm^{-1}) shows nanowires or nanorods morphology and the PANI-ES prepared with the second set of solvents with lower conductivity (<0.3 S cm^{-1}) shows agglomerated spheres or particles morphology.

Conductivity measurement by four-probe method on polymer pellets by the following equation.

$$\sigma = \frac{1}{2\pi RS}$$

Here, the distance between the two points is equal. Where, σ is Conductivity in S cm^{-1}, R= I/V, I is the current flowing through the sample, V is produced the voltage across two inner points, and S is theprobe spacing about ~0.2mm.

Conductivity measurement by a two probe method by the following equation

$$\sigma = \frac{l}{\pi r^2} \times \frac{1}{R}$$

Where l is the thickness in cm, r is the radius in cm and R is the resistance of the pellet in Ω.

Morphology and conductivity are important phenomenal in PANI systems.In this work,we notified morphologies and conductivity tuning with solvents.These results in signpost solvent choosing also important factor prepare of emeraldine PANI systems.

Conclusion

In conclusion, emeraldine form of PANI either in salt or base form could be found from the FT-IR spectrum without conductivity measurement. In this work, PANI-ES systems were prepared without acid in two sets of solvents. A correlation between FT-IR spectral peaks and conductivity level of emeraldine PANI system was established. Also, FT-IR spectral peaks could be used to indicates the type of method of conductivity measurement i.e., either two probe or four probe techniques. The peaks observed at lower wave number in FT-IR spectrum for the higher conductivity PANI-ES (>0.3 S cm^{-1}) compared to the lower conductivity PANI-ES (<0.3 S cm^{-1}). The scope of this work is to indicate that FT-IR spectrum could be used to find out the conductivity level of PANI-ES samples and its measurement technique, i.e. either using ordinary multimeter with two probes or four probes measurement.

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Conflict of Interest

The author(s) declare(s) that there is no conflict of interests regarding the publication of this article.

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