

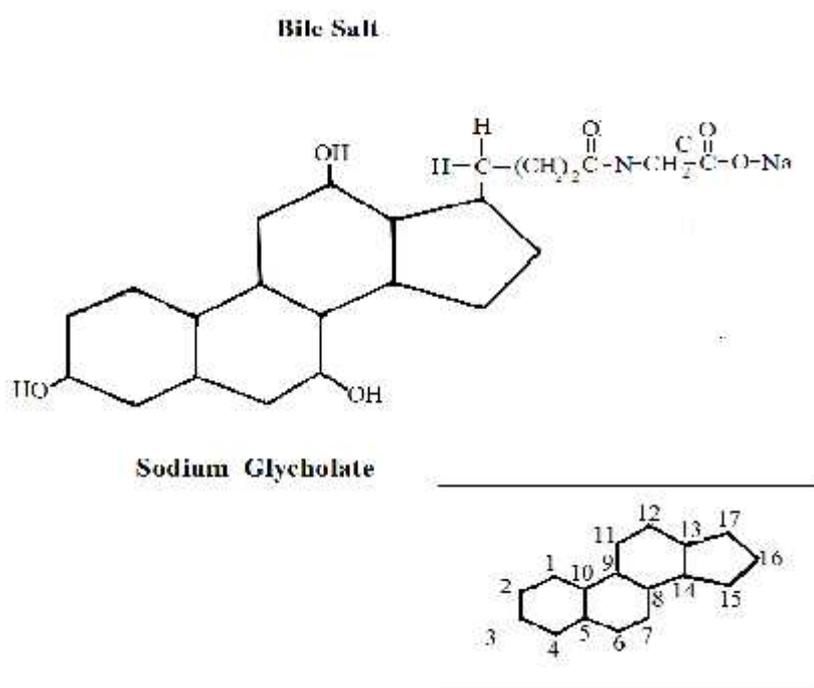
## Chapter 4

### Bile salt incorporated Polypyrrole for ethanol sensing

#### 4.1 Introduction

Polypyrrole (PPy) has been extensively used for bio-molecule incorporation due to its environmental stability and ease of fabrication, in addition to other conventional novel properties of its kind [1]. Fixation of an enzyme in the polymer matrix of PPy by membrane confinement has been shown to increase its electrical and mechanical properties also [2-3]. Being highly effective and specific under ambient conditions, enzymes are generally used as bio - catalysts that enhance the rate of reaction by lowering the surface activation energy [4]. But they are mostly stable at low temperatures and neutral pH only and the stability can be easily disturbed by external pressure and temperature, extreme pH, organic solvents, freezing, drying and oxidative chelating or denaturing agent [5]. However, these inherent problems of enzyme immobilization in external environment can be reduced with their derivatives. Choline Oxidase (ChOX) is an enzyme which shows sensing properties when immobilized in a conducting polymer [6]. Bile salt is a derivative of Cholic Acid which we used here as a substitute of ChOX to incorporate in PPy during its oxidative polymerization. Bile salts have a unique molecular structure and are usually derived from a saturated tetra cyclic hydrocarbon, perhydro-cyclopentano-phenantherene system [7], which is a steroid. It can be obtained as derivative of Cholic Acid also. Cholic Acid, as already elaborated in the previous chapter is a lipophilic compound and this property is exhibited by its different derivatives also [8]. However, there is a marked difference in the balance between hydrophilic and hydrophobic character of different molecular species in bile salt which accounts for the difference in its interaction with other substances [9], e.g. cholesterol, lipids, alcohols etc.

The hydrophilicity of conjugated bile salts decreases in the order Ursodeoxycholic Acid > Cholic Acid > Chenodeoxycholic Acid > Deoxycholic Acid > Lithocholic Acid > Glycyl conjugate > Free species [9]. This balance can be modified by attachment of a particular molecule. On this background we used bile salt to incorporate in the chemical polymerization of Pyrrole and found that incorporation of bile salt in PPy considerably modified its surface properties, which were manifested in sensing behavior of the polymer composite when exposed to ethanol vapor. The results obtained are found superior to those obtained with incorporation of Cholic Acid discussed in previous chapter. Improved conductivity due to increased electronic mobility on ethanol exposure was supposed to be caused by modification of the PPy backbone in the later case [10-12]. Structure of the Na-derivative of bile salt incorporated as a pendant group in the PPy backbone during its polymerization is shown in Fig. 4.1 below.



**Fig 4.1 Structure of Na-derivative of bile salt (Inset: C-atom)**

## 4.2 Experimental

Polypyrrole (PPy) is prepared by interface polymerization method using toluene-water interface, by taking 1 M pyrrole in toluene and 1 M FeCl<sub>3</sub> in aqueous solution of 1 M HCl [13-14]. PPy membrane formed at the interface is immediately taken out, dried and repeatedly washed with deionized water and methanol to remove any un-reacted oxidant and oligomers, and then dried again. PPy-bile salt composite is prepared by dispersing the dried PPy in an aqueous solution of bile salt. The ratio of bile salt to PPy is kept at weight proportion of 1:10. The resultant solution is then subjected to magnetic stirring at room temperature. The composite film is prepared by spin casting the resultant dispersion on glass substrate and dried under vacuum. The other set of similar films are exposed to ethanol vapor at 310 K for three different response times of 30, 45, 60 and 90 s. Both the films are characterized using the equipments elaborated in Chapter 2.

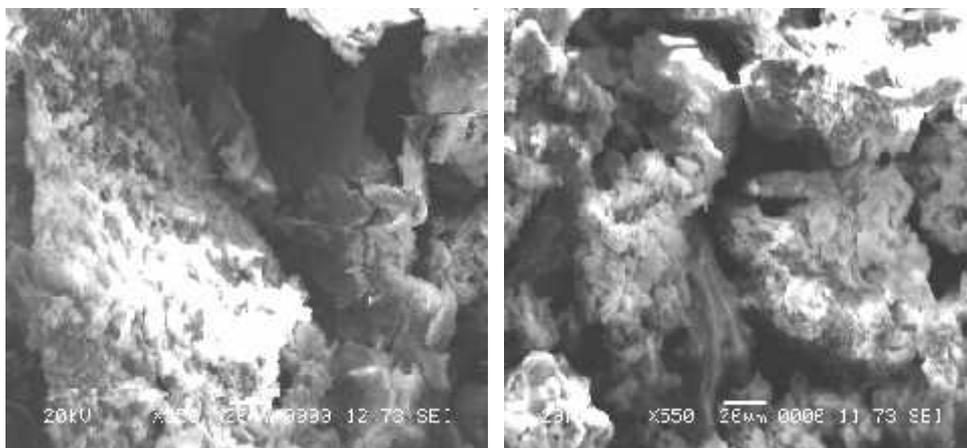
Characterization is done by SEM, FTIR, PL, NMR and XRD. Molecular weight is determined by GPC. Electrical properties are studied by current-voltage (I-V) measurements in the dc voltage range of -20 to +20 V.

## 4.3 Results and discussion

### 4.3.1 Surface morphology

The morphology of the films observed through SEM micrographs is shown in Fig. 4.2 for untreated PPy-bile salt composite (a) and also for the treated one (b).

Micro shaped particles are observed in both the samples indicating the characteristic bulk phase of the material.



**Fig. 4.2 SEM image of the composite (a) Unexposed (b) exposed**

Both the films show agglomeration and aggregation of particles which is more significant in the ethanol treated one. They suggest binding of bile salt to the PPy chain leading to a ‘microstructure’ particularly in case of the ethanol treated one [15].

#### **4.3.2 FT-IR study**

The molecular structure of PPy composites are studied through FTIR spectroscopy. The FTIR spectra of the two types of films are shown in Fig. 4.3. It is found that in addition to the characteristic PPy bands in the region of  $2500\text{-}3400\text{ cm}^{-1}$ , there are additional bands at  $1400$ ,  $726$  and  $474\text{ cm}^{-1}$  indicating the presence of C–N, =C–H and carboxylic/amino groups respectively [16-18].

On ethanol exposure these bands show overall decrease in intensity for almost all bands with nominal shifts in the peak position.

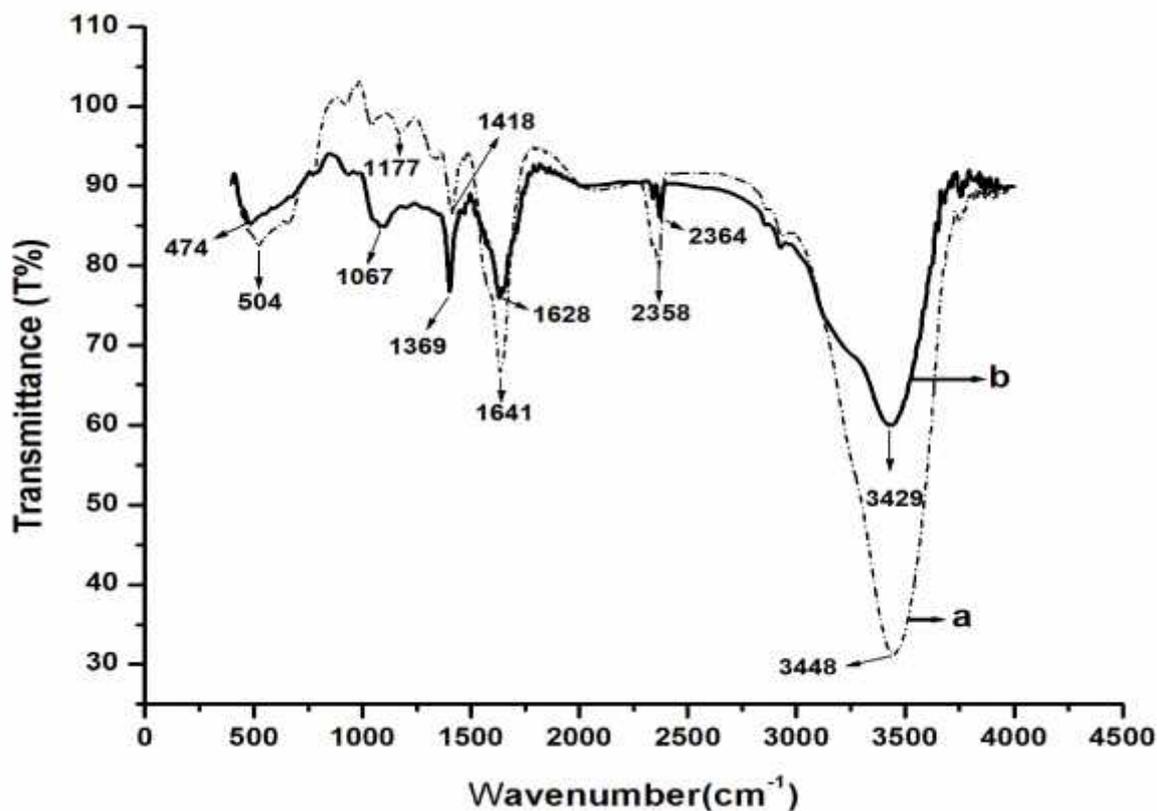
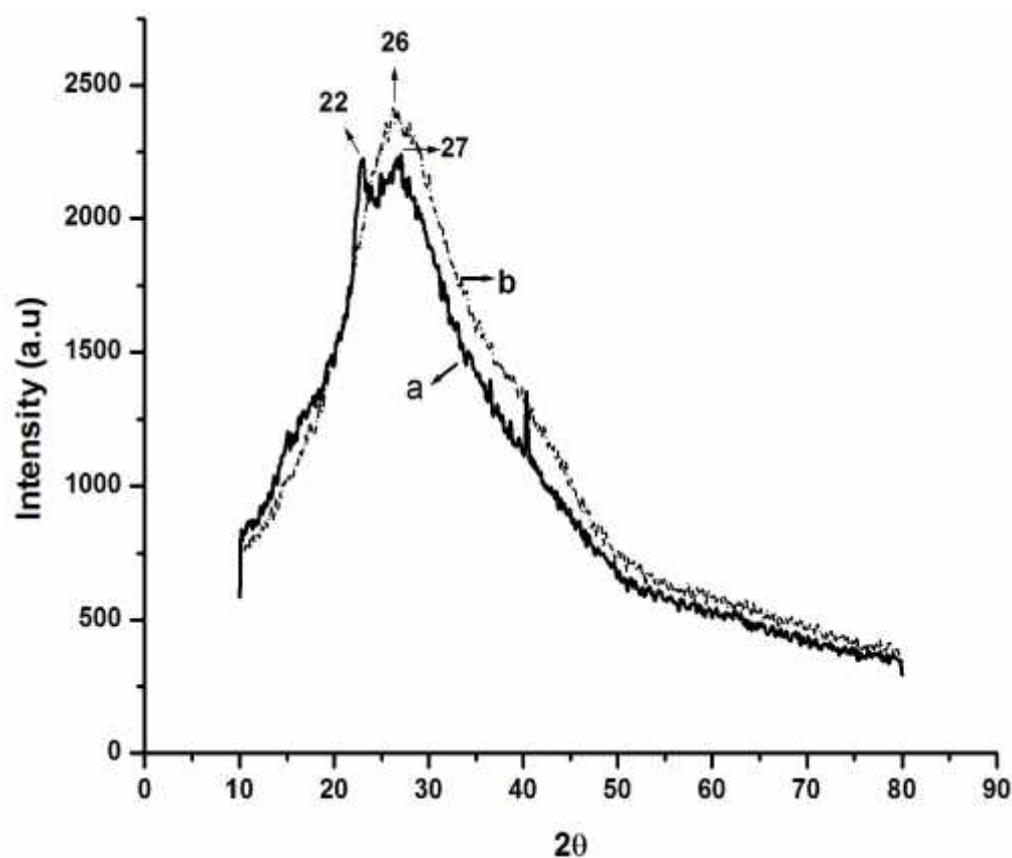


Fig. 4.3 FT-IR profile of the composite (a) Unexposed (b) exposed

### 4.3.3 X-Ray Diffraction study

To observe the possible structural changes on ethanol exposure, XRD studies of the films are carried out, with results shown in Fig. 4.4. The XRD pattern for untreated composite film gives peaks at  $22^\circ$  and  $27^\circ$  respectively indicating the partial amorphous nature of the composite [19-20]. The twin peaks merge when the composite is exposed to ethanol and a

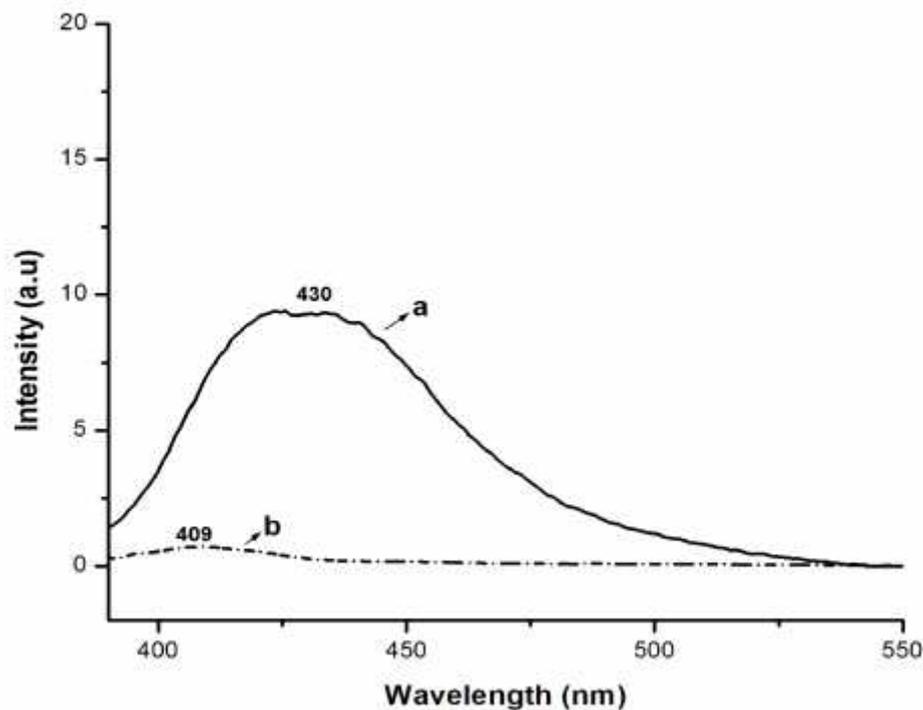
single sharper peak appears at  $2\theta = 26^\circ$ . From this observation, it is inferred that composite molecules are in more ordered state on ethanol exposure, resulting in increased crystallinity [21].



**Fig. 4.4 XRD profile of the composite (a) Unexposed (b) exposed**

#### 4.3.4 Photoluminescence study

PL spectra of the films are studied in order to visualize any possible influence in its optical properties after treatment with ethanol. The room temperature PL spectra for excitation wavelength of 350 nm shows PL quenching in the ethanol treated film (Fig. 4.5) indicating that

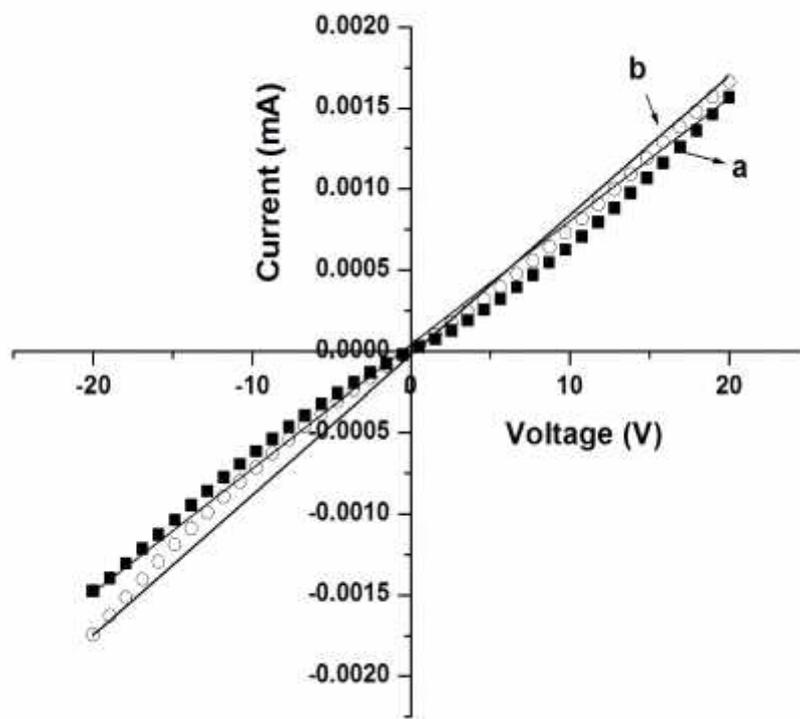


**Fig. 4.5 PL profile of the composite (a) Unexposed (b) exposed**

the molecular binding of ethyl alcohol with the composite creates some intermittent levels in the band gap of the latter. Aggregation of particles after ethanol exposure as seen in the SEM micrographs will lead to a high concentration of luminescent centers leading to resonant energy transfer in which one of the centers (acting as donor) transfers part of its excitation energy (for instance,  $E_3 - E_2$ ) to the other centre (acting as acceptor). From these states a non-radiative relaxation of photon with energies other than  $E_3 - E_0$  will occur. In any case,  $3 - 0$  emissions will be quenched.

### 4.3.5 I-V Characteristics

To visualize the effect of sensing through electrical properties, we measure current-voltage (I-V) characteristics of both types of the films. The result, depicted in Fig.4.6, shows double non-linear behavior for both of them, but the non-linearity is not that prominent and can be approximated to Ohmic behavior. The slopes of the two curves are measured to be  $7.08539 \times 10^{-5}$  mA/V for the untreated and  $8.0356 \times 10^{-5}$  mA/V for the treated film. In an earlier experiment for determining the electrical properties of PPy composite with polyvinyl alcohol (PVA), we obtained the power law behavior for I-V [13, 22]. This change occurs due to incorporation of bile salt,

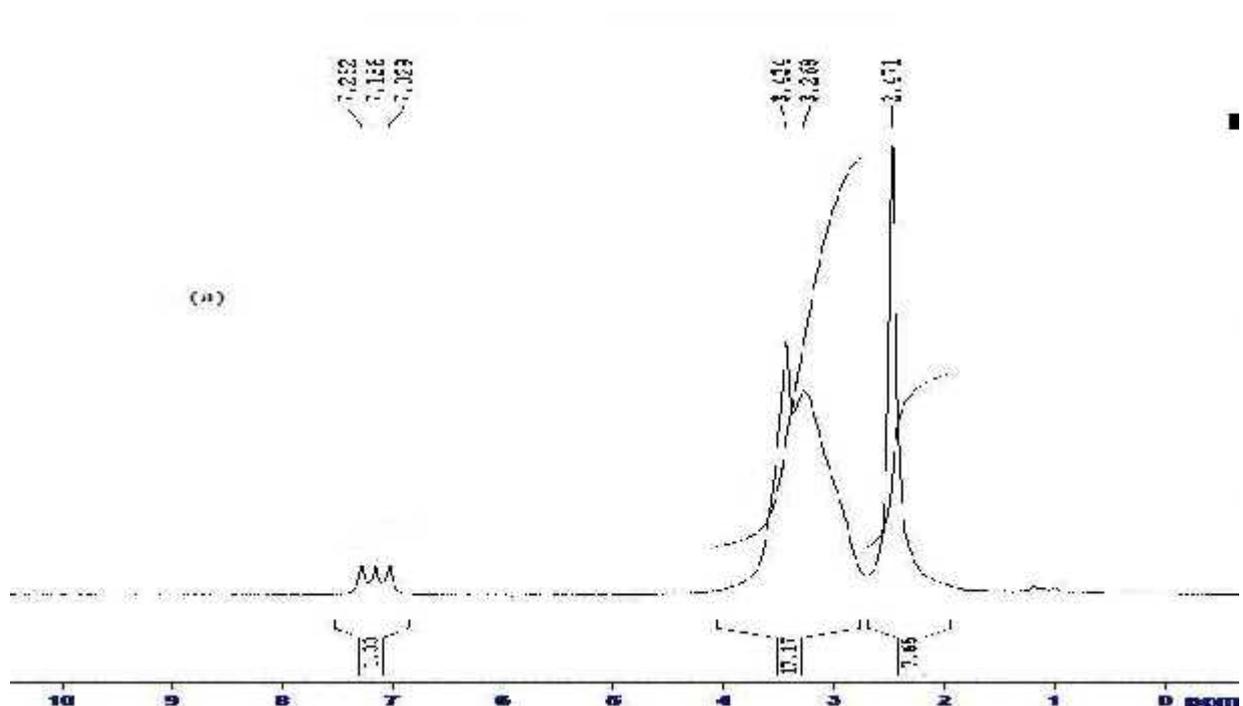


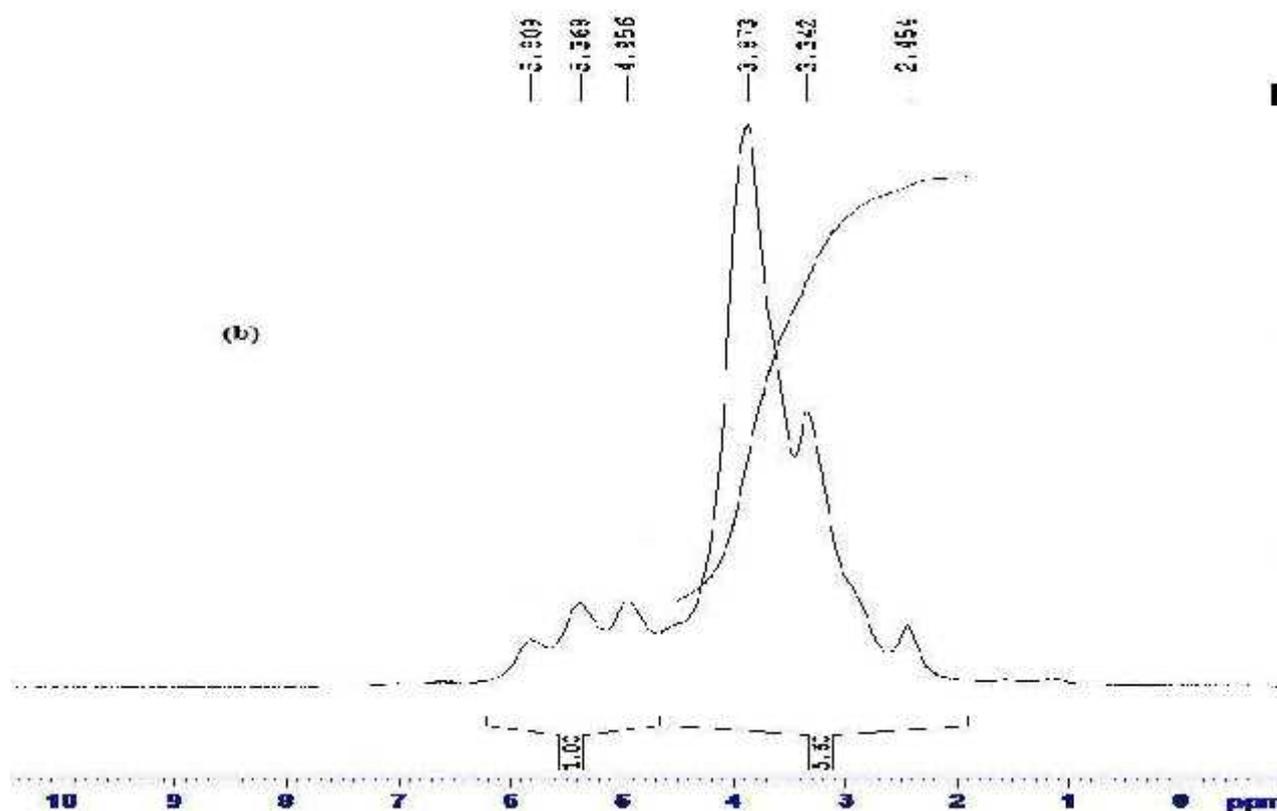
**Fig. 4.6** IV characteristics of the composite (a) Unexposed (b) exposed

which acts as a secondary dopant resulting in optimized band gap of PPy composite, and changes its conductivity pattern. This may happen due to the reason that pure PPy with randomly oriented microscopic particles and with weak linkage among the molecules results in relatively lower conductivity and non-Ohmic behavior [23]. But, the presence of bile salt in the composite functioning as secondary dopant helps it to acquire a granular structure leading to improved compactness of the latter [24]. The compactness may further increase with its exposure to ethanol vapor, resulting in stronger coupling through the grain boundaries, ultimately increasing its conductivity and exhibiting near-Ohmic nature in I-V.

#### 4.3.6 NMR Spectroscopy

The  $^1\text{H}$  NMR spectra of PPy and its composite in Fig. 4.7 below show peaks at 3.434 for the unexposed PPy-bile salt composite and is shifted in the exposed state to 3.676, due to additional spin-spin interaction of the later[25].





**Fig.4.7 NMR spectra of the composite (a) Unexposed (b) exposed**

Thus, we can assume that the pyrrole ring experiences a moderately high field shift on incorporation of bile salt, giving rise to chemical shift of the main pyrrole ring, which might undergo a significant structural change when exposed to alcohol vapour [26].

#### 4.3.7 Molecular weight

Molecular weight, determined by GPC is found to increase on exposure to alcohol vapor for both PPy and its composite. Though marginal in PPy, it is significant in case of the composite, when exposed. The number average molecular weight ( $M_n$ ) of PPy in unexposed and exposed states is 26790 and 28780, while its weight average molecular weight ( $M_w$ ) enhances from 26990 to 28780 on exposure to ethanol. In case of the composite,  $M_n$  changes

from 26160 to 30300 while  $M_w$  changes from 26220 to 30940 respectively, in the unexposed and exposed states. It is probably because of higher degree of absorption of ethanol vapor by the composite, while pure PPy has a lower absorption rate for the same response time. FTIR and NMR analysis also show changes in molecular structure of the composite with further modification on ethanol exposure. So, one can say that the molecular weight obtained in the two states are in conformity with the FTIR and NMR analysis. Further the observed poly disparity, approximately found as unity, indicates the fact that polymerization is completed in one phase and with similar granular sized molecules which is also supported by SEM results discussed in subsection 4.3.1.

#### **4.3.8 Theory of sensing**

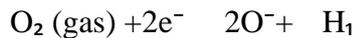
Physical properties of conducting polymers strongly depend on the nature of doping. When a CP composite is brought in contact with a gas or vapor, transfer of electrons takes place between them, which can change the work function of the CP [27]. Thus its resistance also changes which creates a channel for its prospective use in sensing of that gas or vapor.

When electron donating ethyl alcohol vapor is exposed to PPy, its conductance increases. It is observed that pure PPy is more like an insulator but it behaves like a semiconductor in the doped state. The dopant is responsible for modification of the electronic structure of PPy and usually forms additional intermittent energy bands between the valence and the conduction band, reducing the energy gap which finally makes it behave like a semiconductor [28]. Electrical conduction is attributed to the formation of polarons and bipolarons in the doped state.

Earlier studies showed amperometric response of cholesterol oxidase (ChOx) asserted exchange of electron between ChOX and electronegative inorganic salt [29]. Based on this observation, bile salt PPy composite film is exposed to ethyl alcohol vapor for different response times of 30, 45, 60 and 90 sec. It is found that significant change in conductivity of the composite occurs for response time of 45 sec in higher operating voltage. This is due to increased inter-chain conductivity at higher operating voltage [30].

Mechanism of sensing may be explained in two steps in the light of adsorption of ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) over the surface of metal oxide based chemical sensor. The reaction sequence may be written as [31],

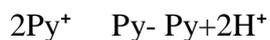
Step I: For sensitizing:



Step II: For detection:



In chemical polymerization of Polypyrrole, Py is monomer and  $\text{Py}^+$  is the radical cation which can dimerise with expulsion of  $\text{H}^+$  in presence of  $\text{FeCl}_3$  which may take the form as,



When the composite is exposed to ethyl alcohol vapour, the gas molecules react with  $\text{O}^-$  ions previously absorbed in the surface as shown in step II, releasing electrons, which increases its conductivity making it a prospective sensing material. The behavior is Ohmic in nature at a high voltage when the catalytic action of bile salt is triggered to break the bipolarons in the PPy composite, forming a layer of free electrons which mainly comes on the surface and

enhances the conductivity of the material. Incorporation of bile salt results in shifting of peaks for H-bonding in FTIR spectra due to exchange of active protons in OH and NH. Increase in conductivity at higher operating voltage may cause enhancement of H<sup>+</sup> ions formation in the composite, where bile salt may be acting as a catalyst in the operating voltage range. Bile salt being basic in nature with optimum pH between 7-9, becomes electro active at a higher voltage.

#### **4.4 Conclusion**

Ethanol sensing of PPy-bile salt composite is tested using morphological, structural, optical and electrical properties. SEM and FTIR results indicate incorporation of bile salt and alcohol in the composites. Sensing is visualized by remarkable change in XRD pattern, leading to merging of peaks and increase of crystallinity in the ethanol treated film. The increase in relative molecular weight due to exposure of ethanol vapor on the composite supports the observations made in other characterizations on morphology and structural properties. PL spectra also show the signature of sensing by significant inhibition of PL intensity in the treated film. The results indicate potential use of the composite as a material for sensing of ethanol in vapor state.

## 4.5 References

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