Chapter-3

Synthesis, characterization, electrical and dielectrical studies of Polypyrrole-Sn(IV)arsenotungstate nanocomposite ion-exchange membrane: Its selectivity as Ba(II)
3.1. Introduction

Membrane can be defined as an interface between two neighbouring phases functioning as a selective obstacle, and at the same time establishing a system into partitions and regulating the transport between two partitions [1]. The promising outcome of membrane technology is its unique selectivity for a particular metal ions, i.e. the transport selectivity of the membrane.

In recent years ion exchange membranes attracted the scientific world as well as industrial world due to their multipurpose applications such as purification of protein, desalination of salt-rich water, removal of hazardous contents from water, industrial waste water treatment plant, food production process etc., usually it requires precise membrane properties for different applications.[2-6] Also, attention is required for electro driven processes such as electro dialysis (ED) for desalination of salt-water.

The ion exchange membranes are likely to have high permselectivity, excellent conductivity, and good chemical, thermal and mechanical stabilities, but maximum polymer based ion exchange membranes are still inadequate for the desalination process. Therefore, the idea in designing composite membranes with the help of inorganic material and organic polymer matrix turn into a tactical implement for the development of new composite ion exchange membranes. The hybrid membranes are likely to hold better strength than the inorganic materials and enhanced electrical conductivity with minimised effects on other properties such as ion-exchange capacity, and functionalities of the polymer matrix.

The mechanism of gas or vapour sensing not only based on ion exchange phenomenon but also depend on electrical properties of the materials. Therefore dielectric properties, AC conductivity, DC conductivity of these materials are an essential part of the characterization of these materials. A commercial polymer, polypyrrole, known as a high performance polymer possessing excellent chemical, thermal and mechanical properties at low cost [7] was selected as the polymer matrix of the ion-exchange membranes.

In view of above facts, present research work, Polypyrrole Sn(IV) arsenotungstate (Ppy-SnAT), a class of organic–inorganic composite ion exchange membrane was prepared, characterized and applied to fabricate Ba(II) selective membrane electrode for electro analytical studies.
3.2. Experimental

3.2.1. Chemicals, reagents and instruments

Pyrrole monomer from spectrochem, iron(III)chloride (Merck, 98%), HCl (35%) from E-Merck (India Ltd.) were used. Sodium arsenate (Finar reagent), sodium tungstate (CDH), Stannic chloride (SnCl$_4$.5H$_2$O) (CDH), methanol from CDH (India Ltd. 98%), polyvinylchloride (PVC) and Demineralised water (DMW) were used in the experimental work. All other reagents and chemicals were of analytical grade.

The following instruments were used; FTIR spectrophotometer (Perkin-Elmer, USA, model Spectrum-BX, range 4000-400 nm), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) (LEO 435–VF), thermo-gravimetric analysis (TGA) using thermal analyzer-V2.2A DuPont 9900 and Rigaku X-Ray powder diffractometer with Cu anode (K$_\alpha$ λ=1.54186 A$^\circ$) using a PW, 1148/89 based diffractometer with Cu K$\alpha$ radiations. A digital potentiometer (Equiptronics EQ 609, India); accuracy 1 mV with a saturated calomel electrode was used as reference electrode. Frequency dependent dielectric spectroscopy measurements were performed in the frequency range of LCR meter (Model: Agilent-4285A) also used for electronic studies.

3.2.2. Synthesis of polypyrrole-Sn(IV)arsenotungstate (Ppy-SnAT) composite ion-exchange material

Ppy-SnAT was synthesized by in-situ chemical oxidative polymerization of pyrrole in the presence of Sn(IV)arsenotungstate particles. 2g of Sn(IV)arsenotungstate was dispersed in 200 ml DMW, taken in three necked round bottom flask, and stirred for 30 min with the help of magnetic stirrer. Then definite amount of pyrrole monomer was added and the mixture was stirred for 45 min for the adsorption of pyrrole on the surface of Sn(IV)arsenotungstate particles. After that, a fixed amount of aqueous FeCl$_3$ solution (prepared by dissolving 2 g FeCl$_3$ in 50 ml DMW) was added to the mixture and kept on constant stirring for another 24 h. The resultant mixture turned slowly into black colored slurry indicating the formation of Ppy-SnAT. It was then filtered off, washed thoroughly with DMW followed by fixed amount of methanol to remove was dried in oven at 50°C. Ppy-SnAT composite ion exchanger was prepared. On the basis of high ion exchange capacity (IEC) and sample Ppy-SnAT (P-2) is selected for further studies given in Table 3.1.
3.2.3. Sorption studies
The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions.

The distribution coefficients (K_d values) of various metal ions on Ppy-SnAT composite were determined by batch method in various solvents systems. Various 100 mg sample of the composite exchanger beads in the H^+ form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and the mixture was kept for 24h.

The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005M solution of EDTA [8], some heavy metal ions such as [Pb^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Ba^{2+}] were determined (Table 3.2). The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase, or in other words, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and can be mathematically calculated using the formula:

\[ K_d = \frac{(I - F)}{F} \times \frac{V}{M} (mlg^{-1}) \]

(1)

Where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of nanocomposite cation exchanger (g).

3.2.4. Synthesis and Characterization of polypyrrole-Sn(IV)arsenotungstate (Ppy-SnAT) composite ion-exchange membrane
For the preparation of ion-exchange membrane, Coetzee and Benson [9] procedure was employed to electro-active material Ppy-SnAT nanocomposite cation exchanger.

To find out the optimum membrane composition, different amounts of the cation exchanger were ground to fine powder [10] and mixed thoroughly with fixed amount of PVC and THF on stirring for 48 h. In this way, four membranes of different thickness i.e. 0.13, 0.17, 0.18 and 0.26 were obtained and the conditions of preparation and IEC of the membranes are given in Table 3.3.
Table 3.1. Synthesis and IEC of Ppy-SnAT nanocomposite cation exchanger.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sn(IV)arsenotungstate Inorganic ion exchanger (gm)</th>
<th>Pyrrole monomer in ml</th>
<th>FeCl3 (Water)(gm)</th>
<th>IEC meq/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2.50</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>1.20</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>9</td>
<td>2</td>
<td>0.80</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>3</td>
<td>2</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 3.2. $K_d$ values of some metal ions on Ppy-SnAT composite in different solvent systems

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Cu$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Hg$^{2+}$</th>
<th>Ba$^{2+}$</th>
<th>Cd$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M HNO$_3$</td>
<td>1050</td>
<td>385</td>
<td>900</td>
<td>337</td>
<td>1125</td>
<td>900</td>
</tr>
<tr>
<td>0.01M HNO$_3$</td>
<td>1500</td>
<td>400</td>
<td>1650</td>
<td>214</td>
<td>4800</td>
<td>540</td>
</tr>
<tr>
<td>0.001M HNO$_3$</td>
<td>2250</td>
<td>260</td>
<td>1100</td>
<td>540</td>
<td>4500</td>
<td>900</td>
</tr>
<tr>
<td>0.1M H$_2$SO$_4$</td>
<td>1300</td>
<td>600</td>
<td>1300</td>
<td>342</td>
<td>1524</td>
<td>1000</td>
</tr>
<tr>
<td>0.01M H$_2$SO$_4$</td>
<td>2400</td>
<td>975</td>
<td>975</td>
<td>334</td>
<td>2100</td>
<td>480</td>
</tr>
<tr>
<td>0.001M H$_2$SO$_4$</td>
<td>1200</td>
<td>550</td>
<td>1350</td>
<td>240</td>
<td>4800</td>
<td>600</td>
</tr>
<tr>
<td>0.1M HCl</td>
<td>2100</td>
<td>470</td>
<td>720</td>
<td>187</td>
<td>4500</td>
<td>675</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>900</td>
<td>900</td>
<td>900</td>
<td>214</td>
<td>1800</td>
<td>420</td>
</tr>
<tr>
<td>0.001M HCl</td>
<td>1000</td>
<td>375</td>
<td>780</td>
<td>210</td>
<td>4200</td>
<td>450</td>
</tr>
<tr>
<td>DMW</td>
<td>1500</td>
<td>750</td>
<td>780</td>
<td>257</td>
<td>3900</td>
<td>540</td>
</tr>
</tbody>
</table>
Table 3.3. Condition of preparation and IEC of Ppy-SnAT ion exchange membrane

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Composites (gm)</th>
<th>Binder Poly vinyl chloride(PVC)(gm)</th>
<th>Stirring time (hours)</th>
<th>IEC of membrane (Meq g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.2</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
<td>0.2</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0.2</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.2</td>
<td>25</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 3.4. Percent composition of Ppy-SnAT composite ion exchange membrane

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Elements</th>
<th>Percentage %</th>
<th>Ppy-SnAT ion exchange membrane</th>
<th>Ba²⁺ adsorbed Ppy-SnAT ion exchange membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>43.90</td>
<td>53.22</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>N</td>
<td>4.39</td>
<td>10.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>21.00</td>
<td>17.00</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fe</td>
<td>0.96</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Sn</td>
<td>13.83</td>
<td>8.86</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>As</td>
<td>5.91</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>W</td>
<td>0.9</td>
<td>6.18</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ba</td>
<td>-</td>
<td>1.05</td>
<td></td>
</tr>
</tbody>
</table>

To know the surface morphology, elemental analysis, thermal stability, crystalline structure and functional group orientation in the composite ion exchange membrane, it
was characterized by some instrumental techniques like SEM, EDX, TGA, XRD and FTIR. Energy-dispersive X-ray (EDX) (Table 3.4)

Physicochemical characterization is also important to understand the performance of composite ion exchange membrane. Thus some parameters such as porosity, water content, swelling, and thickness were determined after conditioning of the composite ion exchange membrane as given in Table 3.5. On the basis of low thickness and IEC membrane M-3 (0.13mm thickness) was selected for further studies.

**Table 3.5. Physiochemical Characterizations of Ppy-SnAT ion exchange membrane**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Thickness of the membrane (mm)</th>
<th>Porosity</th>
<th>Water content as % weight of wet membrane</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.18</td>
<td>0.0324</td>
<td>0.1880</td>
<td>0.038</td>
</tr>
<tr>
<td>2</td>
<td>0.17</td>
<td>0.0563</td>
<td>0.2857</td>
<td>0.048</td>
</tr>
<tr>
<td>3</td>
<td>0.13</td>
<td>0.024</td>
<td>0.0952</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>0.26</td>
<td>0.0456</td>
<td>0.3233</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**3.2.5. Fabrication of ion-selective membrane electrode**

The membrane sheet of Ppy-SnAT cation exchange membrane (0.13 mm thickness) as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as reference) towards which the membrane is selective and kept in an identical solution of the same ion at room temperature. In case of Ppy-SnAT nanocomposite ion-selective membrane electrode, the glass tube was filled with 0.1M Ba(NO₃)₂ solution. Saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:
Following parameters were evaluated to study the characteristics of the electrode such as; lower detection limit, electrode response curve, response time, transport number, working pH range, selectivity coefficient and potentiometric titration.

3.2.6. Electrode response or membrane potential

The response of the electrode in terms of the electrode potential (at 25±2 °C), corresponding to the concentration of a series of standard solutions of Ba(NO₃)₂ (10⁻¹ to 10⁻¹⁰M), was determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [11]. Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

3.2.7. Transport Number

Transport number of Ba(II) ions in the Ppy-SnAT cation exchange membrane was calculated by using the following equation 2.

$$V_M = (2\bar{t}_{Ba(II)} - 1)RT/F \ln[C_2]/[C_1]$$

Where $V_M$ = Electrode potential of the membrane,

$\bar{t}_{Ba(II)}$ = Transport Number,

$C_2$ = Higher concentration of selected solution of Ba(II)

$C_1$ = Lower concentration of selected solution of Ba(II)

3.2.8. Effect of pH

A series of solutions ranging from pH 1-10 were prepared at constant ion concentration i.e $(1 \times 10^{-1}M)$. The pH variations were brought about by the addition of dilute acid (HCl) and alkali (NaOH) solution. The value of electrode potential at each pH was recorded and plotted against pH.
3.2.9. Response time
The response time was measured by recording the EMF of both the electrodes as a function of time when it was immersed in the solution to be studied. The method of determining the response time in the present work is outlined as follows:
The electrode is first dipped in a $1 \times 10^{-1}$M solution of the ion concerned and immediately shifted to another solution (pH~4) of $1 \times 10^{-2}$M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second that is just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 5s. The potentials were then plotted vs. the time. The time during which the potentials attain a constant value represent the response time of the electrode.

3.2.10. Potentiometric titration
The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of a 0.01M Ba(NO$_3$)$_2$ solution against an EDTA solution as a titrant. Potential values were plotted against the volume of EDTA used.

3.2.11. Selectivity coefficient
The response for the primary ion in the presence of other foreign ions is measured in terms of the Potentiometric selectivity coefficient using mixed solution method [12] (Table 3.6). The selectivity coefficient was calculated using the equation given below:

$$K^{\text{POT}}_{AB} = \frac{a_A}{(a_B)^{z_A / z_B}}$$

(3)

Where $a_A$ and $a_B$ are activities of primary and interfering ion of varying concentration of primary ions and fixed concentration of interfering ions and $z_A$ and $z_B$ are charges on the ions.

3.2.12. Dielectric properties of Ppy-SnAT cation exchange membrane
The dielectric properties of Ppy-SnAT cation exchange membrane were measured using frequency range of 75 kHz to 5 MHz using LCR meter (Model: Agilent-4285A) LCR meter at testing temperature ranged from 40 to 60 °C.
Table 3.6. The selectivity coefficient of various interfering ions for Ba$^{2+}$ selective Ppy-SnAT composite cation exchanger membrane

<table>
<thead>
<tr>
<th>Interfering ions (M$^{n+}$)</th>
<th>Selectivity coefficients (K_{MSM})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$^{2+}$</td>
<td>1</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>7.17×10^{-1}</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>7.3×10^{-1}</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>8.3×10^{-1}</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>9.8×10^{-1}</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>9.9×10^{-1}</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>6.96×10^{-1}</td>
</tr>
</tbody>
</table>

3.3. Result and discussion

Ppy-SnAT composite ion-exchange materials were prepared by in-situ polymerization. The Ppy-SnAT composite ion-exchange possessed IEC for Na$^+$ equal to 2.50 meqg$^{-1}$ [Table 3.1]. It is quite evident from the results that the IEC decreased with the increase of pyrrole monomer. In order to explore the potentiality of the material in the separation of metal ions, distribution studies for metal ions were performed in different solvent systems. It is apparent from the data given in [Table 3.2] that the $K_d$-values can vary with the composition and nature of the contacting solvents. It was observed from the $K_d$-values in DMW and other solvent systems that Ba(II) is strongly adsorbed where as Pb(II), Hg(II), Cu(II), Ni(II), Cd(II), comparatively show low adsorption on surface of composite ion exchange material. The high uptake of certain metal ions demonstrates not only the ion-exchange properties but also the adsorption and ion-selective characteristics of the cation-exchanger. The difference in adsorption behavior in different media is largely explained on the basis of differences in the stability constants of the metal-exchanger complexes.
A number of samples of Ppy-SnAT composite ion-exchange membrane were prepared with 500mg, 700mg, 900mg, 1000mg of material with fixed amount of binder (200mg PVC) and fixed amount of THF (25ml) and samples were checked for the mechanical stability, surface uniformity, materials distribution, cracks and thickness, etc. The IEC of different ratio composite ion-exchange membranes for Na⁺ were found 0.6, 0.12, 0.89 and 0.55 meqg⁻¹ respectively. Conditions of preparation and IEC of composite ion-exchanger membrane are given in Table 3.3.

Fig. 3.1 shows the SEM images of Ppy-SnAT and Ba(II) absorbed Ppy-SnAT composite ion-exchange membrane at different magnifications. It is observed that the prepared polymeric composite ion-exchange membrane is porous in nature and forms dense membrane. Fig. 3.1 c and d shows clear absorption of Ba(II) in the pores of Ppy-SnAT composite membrane.

Fig 3.2 shows the elemental composition of the prepared membranes as seen in EDX spectra of Ppy-SnAT nanocomposite membrane (as prepared) and Ba(II) adsorbed composite membrane.

FTIR spectra of Ppy-SnAT ion exchange membrane and Ba(II) adsorbed membrane are presented in Fig. 3.3. For Ppy-SnAT ion exchange membrane, the two bands at 2870 and 2790 cm⁻¹ are due to the symmetric deformation of C-H stretching [13]. Another two bands at 1760 and 1600 cm⁻¹ can be assigned to the C=O stretching and C-C stretching in ring. The bands appearing at 950-700 cm⁻¹ were attributed to C–H vibration due to 1, 2, 4-substitution in the benzenoid rings, and in-plane N-H vibration for amines group respectively. In the FTIR spectra of Ba(II) adsorbed Ppy-SnAT ion exchange membrane indicate that barium metal ion was adsorbed on the surface of ion exchange membrane which may be a weak chemical interaction [14]. The band at 2870 and 2790 cm⁻¹ shifted to 3050 cm⁻¹ and 2950 cm⁻¹, respectively, showing the symmetric deformation of C-H group. A similar peak at 1845 cm⁻¹ as in Ppy-SnAT ion exchange membrane represents C-H vibration frequency. Assemblies of peaks at 950-700 cm⁻¹ were shifted to 1000-700 cm⁻¹ which shows M-O peaks [15].

On the basis of the FTIR and EDX results the schematic representation of the formation of Ppy-SnAT ion exchange membrane is shown in Scheme 3.1. In the synthesis of Polypyrrole the monomer of pyrrole was oxidized to radical cation by using oxidant FeCl₃ by removing one electron to form radical cation [16] after that in step I oxidative-aromatization reaction occurred to form dimer of pyrrole, as in the dimer, there is more conjugation than monomer. Therefore it is more easily oxidized
than the pyrrole monomer and immediately oxidized to cation and proceeds for further polymerization reaction until all of monomers are consumed. This leads to produce the Polypyrrole.

Fig. 3.1. SEM photographs of Ppy-SnAT nanocomposite membrane at different magnifications (as prepared)

Fig. 3.2. EDX photographs of Ppy-SnAT nanocomposite membrane (as prepared) and Ba(II) adsorbed composite membrane
After the oxidation of Polypyrrole in FeCl₃ in aqueous solution, the binding of Polypyrrole into the matrix of Sn(IV)arsenotungstate given as above. In step II, the ion exchange membrane which was adsorbed in Ba(II) metal ion interacted with Ppy-SnAT and formed Ppy-SnAT ion exchange membrane adsorbed in Ba(II).

The TGA curves in Fig. 3.4 show distinct weight losses. In Ppy-SnAT ion exchange membrane the TGA curve shows ~22% weight loss from 50-200 °C which may be due to removal of water molecules and later ~28% decomposition of the membrane at 300 °C and after that a ~18% gradual weight loss was found up to 550 °C, another weight loss (~15%) was observed up to 800 °C. It is quite clear from the results of TGA that Ppy-SnAT ion exchange membrane is thermally stable upto 800 °C.

The X-ray diffraction studies of the Ppy-SnAT (as prepared) and Ba(II) adsorbed Ppy-SnAT ion exchange membrane were carried out using Rigaku X-Ray powder diffractometer with Cu anode (Kα λ=1.54186Å) in the range of 20°≤2θ ≤ 80° at 30Kv. Fig. 3.5 shows the typical XRD pattern of the ion exchange membrane at room temperature. The XRD pattern of Ppy-SnAT composite ion exchanger recorded in powdered sample exhibited no sharp peaks in the spectrum which suggests that the
material is amorphous in nature [17]. In Ba(II) adsorbed Ppy-SnAT ion exchange membrane, a peak is found on 25° due to the incorporation of Ba(II) in to the Ppy-SnAT composite. The presence of this peak suggest the presence of Ba(II) in the sample..

Scheme 3.1. The schematic representation of the formation of Ppy-SnAT ion exchange membrane and Ba(II) adsorbed composite membrane.
Fig. 3.4. TGA photographs of Ppy-SnAT nanocomposite membrane

Fig. 3.5. XRD photographs of Ppy-SnAT nanocomposite membrane and Ba(II) adsorbed composite membrane
Physicochemical characterizations of Ppy-SnAT ion exchange membrane were also essential in making it an ion selective electrode. Thus some properties like swelling, thickness, porosity, water content capacities were determined [Table 3.5].

The Ppy-SnAT ion exchange membrane (thickness 0.18, 0.17, 0.13 and 0.26 mm respectively) was selected for making ion selective electrode. Thus low order of water content, swelling and porosity with less thickness of these membranes suggests that interstices are negligible and diffusion across the membranes would occur mainly through the exchanger sites. So, on the basis of low thickness, porosity and high IEC membrane M-3 was selected for further studies.

Including small amounts of Sn(IV)arsenotungstate in Ppy-SnAT was proved to be advanced approach to improve the properties of Ppy-SnAT ion exchange membrane. The composites statically maintained its mechanical stability and thermal stability excellently although the IEC, permiselectivity of the membranes were enhanced. When Sn(IV)arsenotungstate added with the organic polymer (Polypyrrole) the porosity of the membranes was improved through the particle cluster formation. For ionic species to pass through which are very effective properties for the ion exchange membranes especially the transport phenomena and permeability of the membranes which are due to the porosity and pore sizes of the membranes. For more improvement of the IEC and transport phenomena of the composite ion exchange membrane the control of the pore sizes and pore distribution play very crucial role.

Sensitivity and selectivity of the ion-selective electrode depends upon the nature of electro-active material. When membrane of such materials was placed between two electrolyte solutions of same nature, but at different concentration of metal (to which membrane is selective) ions, the ion exchange diffusion phenomenon predominates, the ions selective to membrane [Ba(II)] were exchanged by the H⁺ present on the surface of the membrane, thus producing an electrical potential difference i.e. membrane potential. The potentiometric response Ppy-SnAT ion exchange membrane electrode (M-3) over a wide concentration ranges $1 \times 10^{-10}$ M to $1 \times 10^{-1}$ M is shown in Fig. 3.6. The electrode shows a linear response in the range of $1 \times 10^{-9}$ M to $1 \times 10^{-1}$ M with an average Nerstian slope of 11.87 mV per decade change in concentrations. The limit of detection was determined from the intersection of the two extrapolated segments of the calibration graph [18] and found to be $1 \times 10^{-9}$ M for Ppy-SnAT ion exchange membrane. Thus, the working concentration range of membrane (M-3) was found to be $1 \times 10^{-9}$ M to $1 \times 10^{-1}$ M for Ba(II).
A plot of transport number verses concentration in Fig. 3.7 was also found in close agreement with working of electrode in the concentration range of $1 \times 10^{-9}$ M to $1 \times 10^{-1}$ M. pH effect on the potential response of the electrode was measured for a fixed ($1 \times 10^{-2}$ M) concentration of Ba(II) ions in different pH values. It is clear that electrode potential remains unchanged within the pH range of 3.0-5.0 (Fig. 3.8) known as working pH range for the electrode.

Response time is another important factor for ion selective electrode. The average response time is defined as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different ion solutions, each having a 10-fold difference in concentration. The response time in contact with $1 \times 10^{-2}$ M Ba(II) ion solution was determined, and the results are shown in (Fig. 3.9). It is clear from the figure, that the response time of the membrane was ~35 s.

The membrane could be successfully used up to 6 months without any notable drift in potential during which the potential slope was reproducible within ±1 mV per concentration decade. Whenever a drift in the potential was observed, the membrane was re-equilibrated with 0.1 M Ba(NO$_3$)$_2$ solutions for 3-4 days.
Fig. 3.7. Plot of transport no. of Ppy-SnAT nanocomposite membrane electrode in aqueous solution of Ba(NO$_3$)$_2$.

Fig. 3.8. Effect of pH on the potential response of the Ppy-Sn(IV)AT nanocomposite membrane electrode.
Fig. 3.9. Time response curve of Ppy-SnAT nanocomposite membrane electrode at $1 \times 10^{-2}$ M Ba(II) concentration

Fig. 3.10. Potentiometric titration of Ppy-SnAT nanocomposite membrane electrode at $1 \times 10^{-2}$ M Ba(II) concentration
Owing to the good selectivity of the Ba(II) selective electrode it has been employed as an indicator electrode for the titration of selective Ba(II) against an EDTA solution as titrant. The addition of EDTA causes a decrease in potential as a result of the decrease in free metal ion concentration i.e. Ba(II) due to its complexation with EDTA (Fig. 3.10). The amount of Ba(II) in solution can be accurately determined from the resulting neat titration curve providing a sharp equivalence point. This study established the practical and analytical utility of the proposed composite cation-exchanger membrane electrode.

The selectivity behaviour was obviously one of the important characteristics of the ion-selective electrodes, determining whether reliable measurement in the target sample was possible or not. It was determined by the mixed solution method (MSM). It is evident from Table 3.6, that most of the interfering ions showed low values of selectivity coefficient indicating no interference in the performance of the membrane electrode assembly. Such remarkable selectivity for Ba(II) over other ions reflects the high affinity of the membrane towards the Ba(II).

3.3.1. Dielectric properties

3.3.1.1. Dielectric constant

The dielectric constant is represented as:

\[ \varepsilon = \varepsilon' - j\varepsilon'' \]  

(4)

The first term is the real part of the dielectric constant and describes the stored energy but the second term is the imaginary part of the dielectric constant, which describes the dissipated energy. The dielectric constants \( \varepsilon' \) and \( \varepsilon'' \) of the materials have been calculated by the relation:

\[ \varepsilon = \frac{C_p t}{A\varepsilon_0} \]  

(5)

\[ \varepsilon'' = \varepsilon \times \text{loss} \]  

(6)

Both real (\( \varepsilon' \)) and imaginary (\( \varepsilon'' \)) part of the dielectric constant of all samples show a sudden decrease at lower frequency and become almost constant or slower decrease at higher frequency (Fig. 3.11). The decrease in the dielectric constant with increasing frequency is due to dielectric relaxation, a phenomenon that tells that the charge carrier localization is not stable and frequency disturbances affect the charge carrier localization [19]. In other words electron hopping mechanism enhanced with a frequency that gives lower dielectric constant.
Fig. 3.11. Variation of real part of dielectric constant with frequency of Ppy-SnAT and Ba(II) adsorbed Ppy-SnAT nanocomposite membrane.

Fig. 3.12. Variation of imaginary part of dielectric constant with frequency of Ppy-SnAT and Ba(II) adsorbed Ppy-SnAT nanocomposite membrane.
Fig. 3.13. Variation of dielectric loss with frequency of Ppy-SnAT and Ba(II) adsorbed Ppy-SnAT.

Fig 3.14. Variation of AC conductivity with frequency of Ppy-SnAT and Ba(II) adsorbed Ppy-SnAT.

The more dielectric constant was showing Ppy-SnAT than Ppy-SnAT adsorbed Ba(II) and it was also observed that dielectric constant increases with an increase in the
ferrite content (Fig. 3.12). This is due to accumulation of charge carriers in the internal surface of Ppy-SnAT adsorbed Ba(II) matrix which can be explained by Maxwell–Wagner–Sillars affects [20]. Thus, according to the Maxwell–Wagner–Sillars model external electric field application provokes the charge carriers that can easily migrate to the grains, but these grains accumulated at the grain boundaries. This process may be related to produce large polarization and high dielectric constant. The high value of dielectric constant was observed at low frequency in the Ppy-SnAT adsorbed Ba(II) and Ppy-SnAT, which was due to the small conductivity of the grain boundary. Also, higher value of dielectric constant here attributed by the interfacial/space charge polarization into the inhomogeneous nature i.e. porosity and grain structure of Ppy-SnAT. The polarization decreases with the increase in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the hopping of electrons between metal ions and Ppy-SnAT adsorbed Ba(II) that cannot follow the alternating field.

### 3.3.1.2. Dielectric losses

The analysis revealed that the Ppy-SnAT adsorbed Ba(II) and Ppy-SnAT exhibited the frequency dependent dielectric losses, although Ppy-SnAT adsorbed Ba(II) and Ppy-SnAT at higher frequency showed the constant behavior of dielectric losses (Fig.3.13). The dielectric losses were also affected by the amount of Ppy-SnAT nano particles in the Ppy-SnAT and were found to be decreased with increases in Ppy-SnAT nanoparticles. The high value of dielectric losses at lower frequency may be attributable to the high resistivity caused by grain boundary. Moreover, the Ppy-SnAT were showing less dielectric losses than Ppy-SnAT adsorbed Ba(II) that revealed the Ppy-SnAT suitable for electronic applications such as fabrication of capacitors [21].

### 3.3.1.3. AC conductivity

Generally, the total conductivity is the summation of the band and hopping parts:

\[
\sigma = \sigma_0 T + \sigma(\omega, T) \tag{7}
\]

The first term is DC conductivity due to the band conduction, it is frequency independent. The second term is the pure AC conductivity due to the electron hopping processes. AC conductivity of Ppy-SnAT were noticed to be higher than that of Ppy-SnAT adsorbed Ba(II). It was observed that the AC conductivity of Ppy-SnAT increases with an increase in the frequency of AC field and at higher it increases rapidly (Fig. 3.14). The Ppy-SnAT adsorbed Ba(II) shows a slow increase in AC conductivity with increases in frequency even at low frequency as compare to Ppy-
SnAT. AC conductivity also increases with increase in the Ppy-SnAT nano particles in the Ppy-SnAT. It was found that the presence of more amounts of Ppy-SnAT nano particles in the Ppy-SnAT causes a more drastic increment in the AC conductivity at high frequency that attributed to the enhanced electron hopping phenomenon [20].

3.4. Conclusions
Including small amounts of Sn(IV)tungstoarsenate in Polypyrrrole Sn(IV)tungstoarsenate was proved to be advanced approach to improve the properties of Ppy-SnAT ion exchange membrane. The composites statically maintained its mechanical stability and thermal stability excellently although the IEC, conductivity, permselectivity of the membranes were enhanced. When Sn(IV)tungstoarsenate added with the organic polymer, the porosity of the membranes was improved through the particle cluster formation. For ionic species to pass through which are very effective properties for the ion exchange membranes especially the transport phenomena and permeability of the membranes which are due to the porosity and pore sizes of the membranes. For more improvement of the IEC, conductivity and transport phenomena of the composite ion exchange membrane the control of the pore sizes and pore distribution play very crucial role. By the characterization of membranes there is the better understanding towards the effect of inorganic materials on organic polymers and their membrane properties and also the correlation among them.

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References


