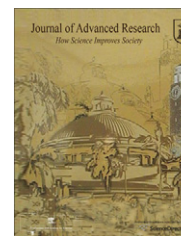Cairo University

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## ORIGINAL ARTICLE

# Preparation and characterization of electrically conducting polypyrrole Sn(IV) phosphate cation-exchanger and its application as Mn(II) ion selective membrane electrode

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**Abstract**  Polypyrrole Sn(IV) phosphate, an organic–inorganic composite cation-exchanger was synthesized via sol-gel mixing of an organic polymer, polypyrrole, into the matrices of the inorganic precipitate of Sn(IV) phosphate. The physico-chemical properties of the material were determined using Atomic Absorption Spectrometry (AAS), CHN elemental analysis (inductively coupled plasma mass spectrometry, ICP-MS), UV–VIS spectrophotometry, FTIR (Fourier Transform Infra-Red), SEM (Scanning Electron Microscopy), TGA–DTA (Thermogravimetric Analysis–Differential Thermal Analysis), and XRD (X-ray diffraction). Ion-exchange behavior was observed to characterize the material. On the basis of distribution studies, the material was found to be highly selective for toxic heavy metal ion $Mn^{2+}$. Due to its selective nature, the material was used as an electroactive component for the construction of an ion-selective membrane electrode. The proposed electrode shows fairly good discrimination of mercury ion over several other inorganic ions. The analytical utility of this electrode was established by employing it as an indicator electrode in electrometric titrations for Mn(II) in water.

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## Introduction

In recent years polymeric–inorganic composites have attracted great interest, both in industry and in academic, because they often exhibit remarkable improvements in material properties when compared with conventional polymers. These improvements can include high moduli [1–6], increased strength and heat resistance [7], decreased gas permeability [8] and decreased flammability [9]. Polymeric–inorganic composite material prepared by incorporation of organic polymer into the inorganic material is the development of a new class of composite used in ion-exchange chromatography. Their chemical,

thermal and mechanical stabilities promote the reproducibility of results obtained from chromatographic studies. A number of such materials were prepared in the laboratory by incorporating, polyaniline, polypyrrole, polyanisidine and poly-o-toluidine into the precipitate of elements of III, IV, V and VI group of the periodic table [10]. These materials were found selective for different metal ions such as $Pb^{2+}$, $Hg^{2+}$ and were applied to making ion-selective membrane electrodes. Electrical conductivity (in semiconducting region) along with the chromatographic behavior of these composites attracted researchers to investigate more possible applications in the field of environmental science engineering [11–13]. Manganese is mainly used in alloys, dry batteries and pigments. Acute exposure to manganese containing dust may lead to chemical pneumonitis, while chronic exposure may lead to a Parkinson-like dementia. Only a few reports on manganese selective electrodes are found in literature. Solid state manganese-selective electrode was prepared in which $Mn_3(PO_4)_2$ was used as an electroactive material and silicon rubber as an inert binder [14]. An electrode with sintered Mn(II) telluride silver sulphide membrane has been reported [15]. The manganese(IV) oxide electrode as a manganese(II) sensor was reported by Midgley and Mulchay [16]. Since Mn(II) is a potential pollutant in the environment, heavy metal ion removal from waste water has been the subject of extensive technological research [17–19].

The ion-exchange membranes obtained by embedding ion-exchangers as electroactive materials in a polymer binder, i.e. epoxy resin PVC, have been extensively used as potentiometric sensors i.e. ion sensors, chemical sensors or, more commonly ion-selective electrodes. In our present studies, an attempt has been made to obtain a new heterogeneous precipitate based membrane electrode by using polypyrrole Sn(IV) phosphate composite cation-exchanger as an electroactive material for the determination of Mn(II) ion present in the sample solution.

## Experimental

### Reagents

The main reagents used for the synthesis of the material were obtained from CDH (India Ltd.), Loba Chemie (India Ltd.), E-merck (India Ltd. Mumbai, India) and Qualigens (India Ltd.), used as received. All other reagents and chemicals were of analytical reagent grade.

### Preparation of polypyrrole Sn(IV) phosphate composite

The composite cation-exchanger was prepared by the sol-gel mixing of polypyrrole, an organic polymer [20] into the inorganic precipitate of Sn(IV) phosphate [21]. Polypyrrole samples were prepared by chemical oxidative polymerization by mixing approximately up to 5% of pyrrole solution (in DMW) dropwise to 0.1 M potassium persulphate solution prepared in 1 M HCl. In this process when the gels of polypyrrole were added to the white inorganic precipitate of Sn(IV) phosphate with constant stirring, the resultant mixture was turned slowly into a brown coloured slurries and kept for 24 h at room temperature.

The polypyrrole based composite cation-exchanger gels were filtered off and, washed thoroughly with demineralized water (DMW) to remove excess acid and any adhering trace

of excess sulphate (from reagent potassium persulphate). The washed gels were dried over $P_4O_{10}$ at 45 °C in an oven. The dried products were immersed in DMW to obtain small granules. They were converted to the $H^+$ form by keeping them in 1 M $HNO_3$ solution for 24 h with occasionally shaking, intermittently replacing the supernatant liquid. The excess acid was removed after several washings with DMW. The material was finally dried at 45 °C and sieved to obtain particles of particular size range ($\sim$125 μm). Hence a number of polypyrrole Sn(IV) phosphate composite cation-exchanger samples were prepared and on the basis of $Na^+$ ion-exchange capacity (i.e.c.), percent of yield and physical appearance, sample S-1 was selected for further studies, see Table 1.

### Ion-exchange capacity (i.e.c.)

The ion-exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process [22].

### Thermal studies

To study the effect of temperature on the i.e.c., 1 g samples of the composite cation-exchange material (S-1) in the $H^+$-form were heated at various temperatures in a muffle furnace for one hour and the $Na^+$ ion-exchange capacity was determined by column process after cooling them at room temperature.

Simultaneous TGA and DTA studies of the composite cation-exchange material (polypyrrole Sn(IV) phosphate, S-1) in its original form were carried out by an automatic thermo balance on heating the material from 10 °C to 1000 °C at a constant rate (10 °C per minute) in the air atmosphere (air flow rate of 400 ml min$^{-1}$).

### Chemical composition

The chemical composition of polypyrrole Sn(IV) phosphate composite cation-exchanger (sample S-1) was determined by elemental analysis of CHN and Sn was determined by AAS (Atomic Absorption spectrometry) while phosphorous was determined by UV-VIS Spectrophotometry.

### Characterization

The FTIR spectrum of polypyrrole (sample S-4), Sn(IV) phosphate (sample S-5) and polypyrrole Sn(IV) phosphate (sample S-1) in the original form dried at 40 °C, were taken by KBr disc method at room temperature. The powder X-ray diffraction (XRD) pattern was obtained in an aluminum sample holder for sample S-1 in the original form using a PW 1148/89 based diffractometer with Cu Kα radiations. Microphotographs of the original form of polypyrrole, (S-4), inorganic precipitate of Sn(IV) phosphate, (S-5), and organic–inorganic composite material polypyrrole Sn(IV) phosphate, (S-1), were obtained by the scanning electron microscope at various magnifications.

### Selectivity (sorption) studies

The distribution coefficient ($K_d$ values) of various metal ions on polypyrrole Sn(IV) phosphate composite were determined

**Table 1** Conditions of preparation and the ion-exchange capacity of polypyrrole Sn(IV) phosphate composite cation exchange materials.

| Sample no. | Mixing volume ratio (v/v) | | | Mixing volume ratio (v/v) | | Appearance of the sample | $Na^+$ ion exchange capacity (meq $g^{-1}$) |
|---|---|---|---|---|---|---|---|
| | $SnCl_4.5H_2O$ in 4 M HCl | $Na_2HPO_4$ 0.1 M DMW | pH | 0.1 M $K_2S_2O_8$ in 1 M HCl | 5% pyrrole solution in DMW | | |
| S-1 | 1 (0.1 M) | 1 (1 M) | 1 | 3 | 1 | Blackish granular | 1.04 |
| S-2 | 1 (0.1 M) | 2 (1 M) | 1 | 3 | 1 | Blackish granular | 0.96 |
| S-3 | 1 (0.1 M) | 1.5 (1 M) | 1 | 3 | 1 | Blackish granular | 0.80 |
| S-4 | – | – | – | 3 | 1 | Black powder | 0.07 |
| S-5 | 1 (0.1 M) | 1 (1 M) | 1 | – | – | White granular | 1.12 |
| S-6 | 2 (0.1 M) | 1 (1 M) | 1 | 3 | 1 | Blackish granular | 0.12 |
| S-7 | 1 (0.1 M) | 1 (0.1 M) | 1 | 3 | 1 | Blackish granular | 0.16 |
| S-8 | 1 (0.2 M) | 1 (0.1 M) | 1 | 3 | 1 | Blackish granular | 0.40 |
| S-9 | 1 (0.2 M) | 1.5 (0.1) | 1 | 3 | 1 | Blackish granular | 0.72 |
| S-10 | 1 (0.1 M) | 1 (0.1 M) | 1 | 3 | 1 | Blackish granular | 0.83 |
| S-11 | 2 (0.1 M) | 2 (1 M) | 1 | 3 | 1 | Blackish granular | 0.89 |

by batch method in various solvent systems [23]. The distribution coefficient ($K_d$) was determined by using the following equation:

$$K_d = \frac{m \text{ moles of metal ions/g of ion} - \text{exchanger}}{m \text{ moles of metal ions/ml of solution}} \text{ (ml } g^{-1}) \quad (1)$$

i.e., $K_d = [(I - F)/F] \times [V/M](\text{ml } g^{-1}) \quad (2)$

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 cation-exchanger (g).

*Preparation of polypyrrole Sn(IV) phosphate cation-exchange membrane*

Ion-exchange membrane of polypyrrole Sn(IV) phosphate was prepared as the method reported by Khan et al. [24] in earlier studies. To find out the optimum membrane composition, different amounts of the composite material were grounded to a fine powder and mixed thoroughly with a fixed amount (200 mg) of PVC dissolved in 10 ml tetrahydrofuran. The resultant slurries were poured to cast into glass tubes 10 cm in length and 5 mm in diameter. These glass tubes were left for slow evaporation for several hours. In this way, three sheets of different thicknesses 0.42, 0.46 and 0.49 mm were obtained. A fixed area of the membranes was cut using a sharp edge blade.

*Characterization of membrane*

The performance of the membrane was checked in terms of the three parameters as reported below [25–27].

*Fabrication of ion-selective membrane electrode*

The membrane sheet of 0.49 mm thickness as obtained by the above procedure was cut in the shape of a disc and mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6) with

araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with 0.1 M manganese nitrate solution. A 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

| Internal reference electrode (SCE) | Internal electrolyte 0.1 M $Mn^{2+}$ | Membrane | Sample solution | External reference electrode (SCE) |
|---|---|---|---|---|

The following parameters were evaluated to study the characteristics of the electrode lower detection limit, electrode response curve, response time and working pH range.

*Electrode response or membrane potential*

To determine the electrode response, a series of standard solutions of varying concentrations ranging from $10^{-1}$ M to $10^{-10}$ M were prepared. The external electrode and the ion selective membrane electrode were plugged into the digital potentiometer and the potentials were recorded.

For the determination of electrode potentials the membrane of the electrode was conditioned by soaking in 0.1 M $Mn(NO_3)_2$ solution for 5–7 days and for 1 h before use. When the electrode was not in use it was kept in 0.1 M $Mn(NO_3)_2$ solution. Potential measurement was plotted against selected concentrations of the respective ions in aqueous solution.

*Effect of pH*

pH solutions ranging from 1 to 13 were prepared at constant ion concentration i.e. ($1 \times 10^{-2}$ M $Mn^{2+}$). The value of electrode potential at each pH was recorded and a plot of electrode potential versus pH was constructed.

*The response time*

The electrode was first dipped in a $1 \times 10^{-3}$ M solution of $Mn(NO_3)_2$ and then in a tenfold higher concentration $(1 \times 10^{-2}$ M). The potential of the solution was read at zero seconds; just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 10 s. The potentials were then plotted vs. time.

*Determination of $Mn^{2+}$ by potentiometric titration's using polypyrrole Sn(IV) phosphate composite membrane electrode*

The practical utility of the proposed membrane sensor assembly was tested by its use as an indicator electrode in the potentiometer titration of Mn(II) with EDTA.

**Results and discussion**

Various samples of a new and novel organic–inorganic composite cation-exchange material have been developed by the incorporation of electrically conducting polymer polypyrrole into the inorganic matrices of fibrous Sn(IV) phosphate. Due to the high percentage of yield, better ion-exchange capacity, reproducible behavior, chemical and thermal stabilities, sample S-1 (Table 1) was chosen for detailed ion-exchange studies.
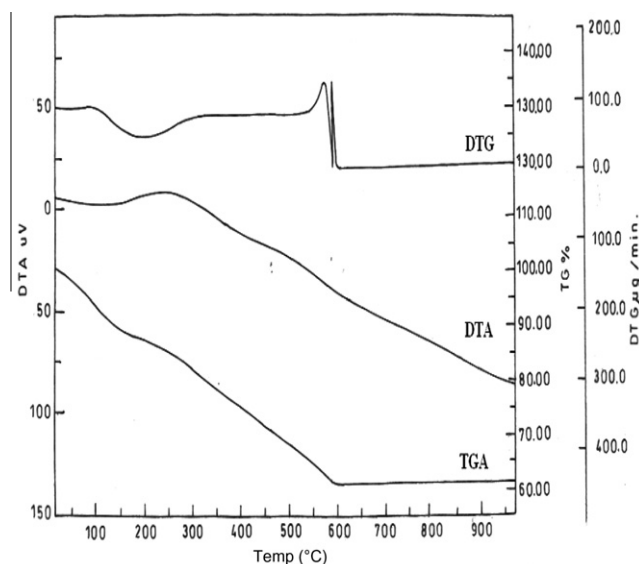


**Fig. 1** Simultaneous TGA–DTA curves of polypyrrole Sn(IV) phosphate (as-prepared).

The composite cation-exchange material possessed a better $Na^+$ ion-exchange capacity (1.04 meq $g^{-1}$) as compared to
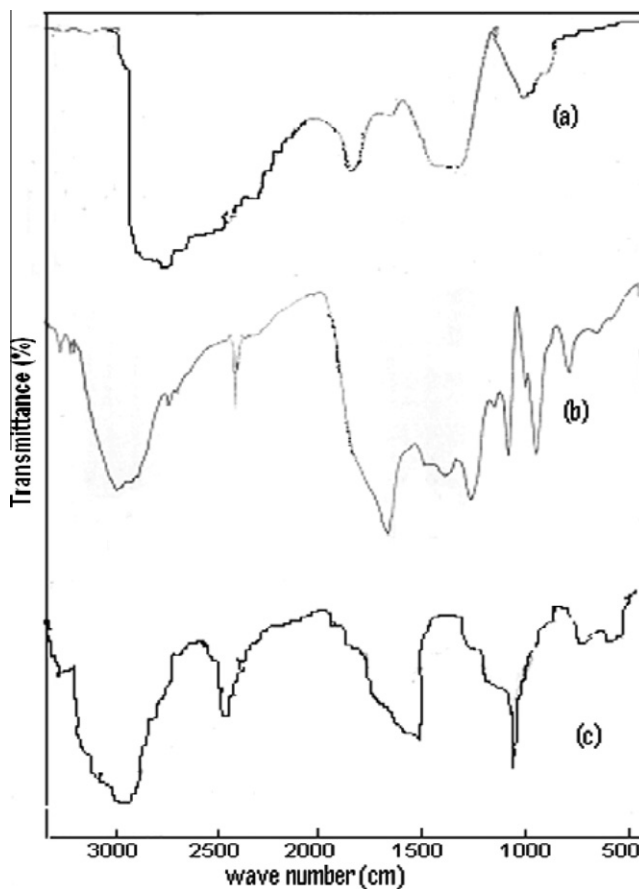
**Table 2** Ion-exchange capacity of various exchanging ions on polypyrrole Sn(IV) phosphate composite cation exchanger.

| Exchanging ions | pH of the metal solution | Ionic radii (A°) | Hydrated ionic radii (A°) | Ion exchange capacity (meq dry $g^{-1}$) |
|---|---|---|---|---|
| $Na^+$ | 4.99 | 0.97 | 2.76 | 1.04 |
| $K^+$ | 6.50 | 1.33 | 2.32 | 0.96 |
| $Li^+$ | 3.30 | 0.68 | 3.40 | 0.40 |
| $Mg^{2+}$ | 4.87 | 0.78 | 7.00 | 0.97 |
| $Ca^{2+}$ | 6.20 | 1.06 | 6.30 | 0.83 |
| $Sr^{2+}$ | 6.02 | 1.27 | – | 0.67 |
| $Ba^{2+}$ | 6.50 | 1.43 | 5.90 | 0.55 |

**Table 3** Effect of temperature on ion exchange capacity of polypyrrole Sn(IV) phosphate composite cation exchanger on heating time for 1 h.

| S. no. | Heating temperature (°C) | $Na^+$ ion-exchange capacity (meq dry $g^{-1}$) | % Retention of ion-exchange capacity |
|---|---|---|---|
| 1 | 100 | 1.04 | 100 |
| 2 | 150 | 0.98 | 94.2 |
| 3 | 200 | 0.76 | 73.0 |
| 4 | 250 | 0.72 | 69.2 |
| 5 | 300 | 0.60 | 57.6 |
| 6 | 400 | 0.48 | 46.1 |
| 7 | 500 | 0.31 | 29.6 |
| 8 | 600 | 0.12 | 11 |
| 9 | 700 | 0.02 | 1.9 |
| 10 | 800 | 0.00 | 0.0 |



**Fig. 2** FT-IR spectra of Sn(IV) phosphate (a), polypyrrole (b) and polypyrrole Sn(IV) phosphate (c) composite.
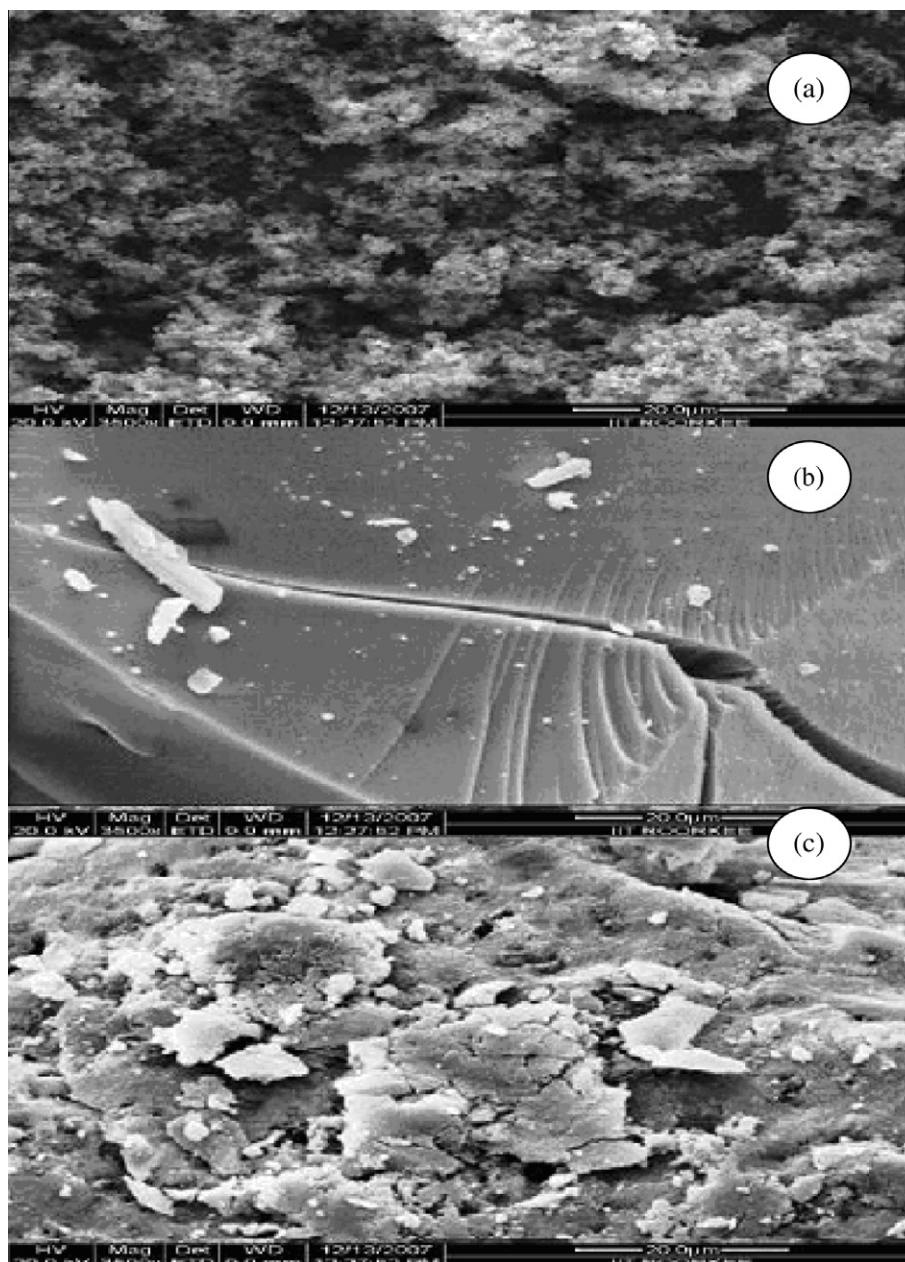
**Fig. 3** SEM photographs of polypyrrole (a), Sn(IV) phosphate (b), and polypyrrole Sn(IV) phosphate (c) composite at the magnification of 3500×.

the inorganic precipitate of Sn(IV) phosphate (0.72 meq g$^{-1}$) [28].

The effect of the size and charge of the exchanging ion on the ion-exchange capacity was also observed for this material. The alkali metals shows a decreasing trend of ion-exchange capacity ($K^+ > Na^+ > Li^+$), while the alkaline earth metal ions follow the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The size and charge of the exchanging ions affect the ion- exchange capacity of exchanger. This sequence is in accordance with the hydrated radii of the exchanging ions (Table 2).

The material was found to possess good thermal stability as it retained about 60% of its ion–exchange capacity upto 300 °C (Table 3).

The solubility experiments showed that the material has good chemical stability. To determine the chemical composition of the composite material, 200 mg of the sample was dissolved in 20 ml of concentrated $H_2SO_4$. The material was analysed for metal ions by ICP-MS and phosphate by the phosphovana-do molybdate method. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The percent composition of C, H, O, N, P and Sn in the material was found to be 13.25, 2.54, 51.77 ± 0.05, 4.10, 2.11 and 26.23, respectively.

*Characterization*

It is clear from the TGA curve of the composite cation-exchanger that up to 100 °C only 6% weight loss was observed, which may be due to the removal of external $H_2O$ molecules present

**Table 4** $K_d$-values of some metal ions on polypyrrole Sn(IV)phosphate composite cation- exchanger column in different solvent systems.

| Solvents | Metal ions | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Zn^{2+}$ | $Cu^{2+}$ | $Cd^{2+}$ | $Mn^{2+}$ | $Mg^{2+}$ | $Co^{2+}$ | $Ba^{2+}$ | $Sr^{2+}$ | $Pb^{2+}$ | $Hg^{2+}$ |
| DMW | 10 | 9 | 1 | 97 | 23 | 21 | 25 | 11 | 14 | 0 |
| $10^{-1}$ M HCl | 2 | 90 | 2 | 150 | 132 | 51 | 34 | 9 | 46 | 24 |
| $10^{-1}$ M HNO$_3$ | 8 | 7 | 4 | 150 | 42 | 11 | 71 | 2 | 46 | 23 |
| $10^{-2}$ M HNO$_3$ | 36 | 100 | 11 | 176 | 100 | 37 | 8 | 40 | 40 | 0 |
| 10%HCOOH | 29 | 96 | 8 | 100 | 28 | 8 | 33 | 19 | 0 | 6 |
| 20% Acetone | 133 | 108 | 5 | 127 | 42 | 34 | 53 | 191 | 0 | 0 |
| Buffer 5.75 | 24 | 107 | 7 | 132 | 100 | 35 | 10 | 94 | 0 | 8 |
| $10^{-2}$ M H$_2$SO$_4$ | 152 | 84 | 10 | 127 | 22 | 92 | 70 | 15 | 67 | 146 |
| $10^{-2}$ M HClO$_4$ | 81 | – | 34 | 77 | 34 | 47 | 68 | 28 | 22 | – |
| 10% Ethanol | – | – | 4 | 24 | 30 | 92 | – | 34 | – | – |

at the surface of the composite [29]. Further weight loss of mass approximately 15% between 100 and 250 °C may be due to the slight conversion of inorganic phosphate into pyrophosphate. Slow weight loss of mass of about 25% between 250 and 600 °C may be due to the slight decomposition of the organic part of the material (Fig. 1).

The FTIR spectra of the composite cation-exchanger, sample S-1 (Fig. 2) indicates the presence of external water molecules in addition to the –OH groups and metal oxides present internally in the material. In the spectrum, a strong broad band around 3400 cm$^{-1}$ was found, which could be attributed to –OH stretching frequency. The peak at 1500 cm$^{-1}$ may be due to interstitial water present in the composite material. The peak at 1080 cm$^{-1}$ may represent the presence of ionic phosphate groups [30] in the material. The small additional band around 1300–1100 cm$^{-1}$ can be ascribed to the stretching vibration of C–N [30]. This indicates that the material contains considerable amounts of pyrrole.
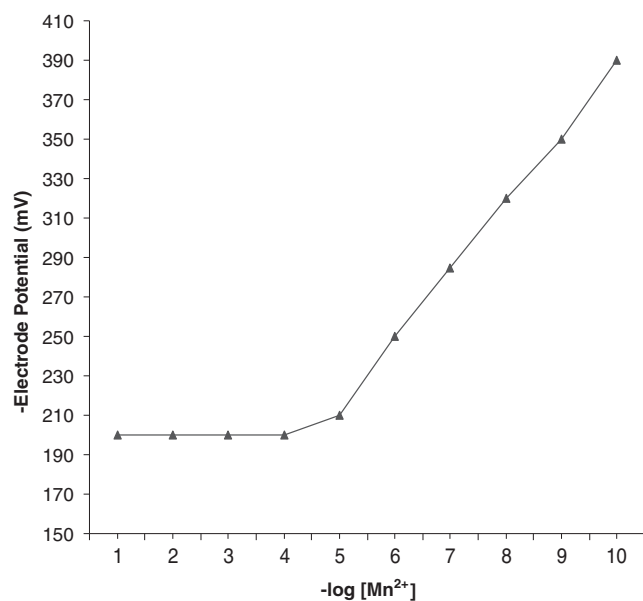


**Fig. 4** Calibration curve of polypyrrole Sn(IV) phosphate membrane electrode in aqueous solutions of Mn(NO$_3$)$_2$.

The X-ray diffraction pattern of these materials (S-1 as prepared) recorded in powdered samples exhibited some small peaks in the spectrum (Fig. not shown), which suggests a semi-crystalline nature of the composite material. The scanning electron microphotograph (SEM) of polypyrrole, Sn(IV) phosphate and polypyrrole Sn(IV) phosphate are represented in Fig. 3. It is clear from the photographs that after the binding of organic polymer polypyrrole with inorganic precipitate of Sn(IV) phosphate, the morphology of the material has been changed with the formation of organic–inorganic composite material polypyrrole Sn(IV) phosphate.

In order to explore the potential of the composite material (S-1) in the separation of metal ions, distribution studies for ten metal ions were performed in ten solvent systems (Table 4). Some factors which affect the distribution coefficient of cations are the charge, size, swellings, formation of complexes, nature of the chemical bond, solvent distribution and nature of the ion exchanger. The main three factors which affect the ability of an ion to compete effectively with another are the charge on the ion, its ionic radii and the hydrated energy of the competing ion. For an ion to be effective in competition reaction its charge and hydration energy must be high and its radius should be small. The small ionic radii of Mn(II) (0.80 Å) as compared to Hg(II) (1.02) and K(I) (1.33), may enable Mn(II) to be attracted more easily by co-ions (phosphates and amines) present in the matrix of the material as compared with other cations. Thus, Mn$^{2+}$ was strongly adsorbed while the rest were partially adsorbed on the surface of ion-exchange material.
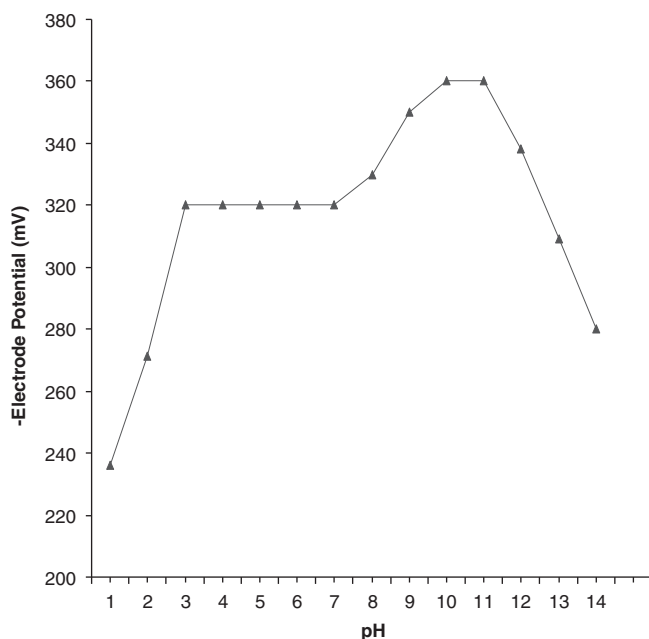
*Preparation of Mn(II) ion-selective membrane electrode*

In this study, organic–inorganic composite cation exchanger polypyrrole Sn(IV) phosphate was also used for the preparation of heterogeneous ion-selective membrane electrodes.

The sensitivity and selectivity of the ion-selective electrodes depend upon the nature of the electro-active material, membrane composition and the physico-chemical properties of the membranes employed. A number of samples of the polypyrrole Sn(IV) phosphate composite membrane were prepared with different amounts of composite material and PVC and was checked for mechanical stability, surface uniformity, materials distribution, cracks and thickness, etc. The membranes obtained with 33% PVC (w/w) (M-1) were found suitable (Table 5).

**Table 5** Characterization of ion-exchange membrane.

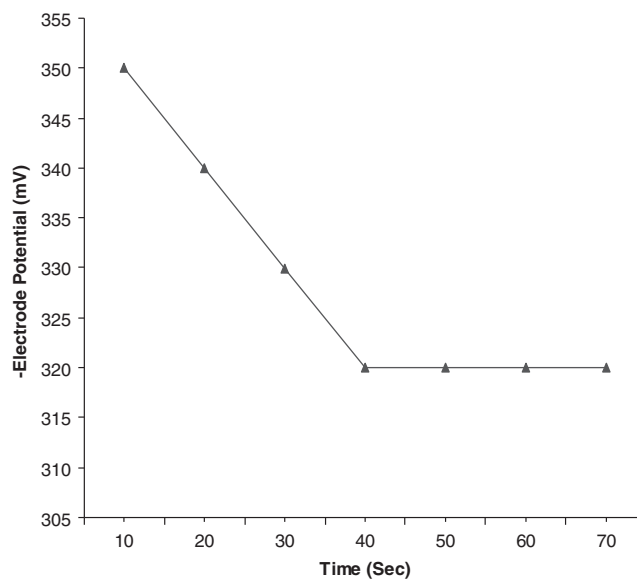| Polypyrrole Sn(IV) phosphate composite material | Thickness of the membrane (mm) | Water content as % weight of wet membrane | Porosity | Swelling of % weight of wet membrane |
|---|---|---|---|---|
| M-1 | 0.42 | 2.135 | 0.002 | 2.326 |
| M-2 | 0.46 | 2.224 | 0.002 | 4.166 |
| M-3 | 0.49 | 1.883 | 0.0015 | 7.500 |



**Fig. 5** Effect of pH on the potential response of the polypyrrole Sn(IV) phosphate membrane electrode at $1 \times 10^{-2}$ M $Mn^{2+}$ concentration.



**Fig. 6** Time response curve of polypyrrole Sn(IV) phosphate membrane electrode.

The heterogeneous precipitate Mn() ion-selective membrane electrode obtained from polypyrrole Sn(IV) phosphate cation-exchanger material gives a linear response in the range $1 \times 10^{-1}$ M and $1 \times 10^{-6}$ M. Suitable concentrations were chosen for the sloping portion of the linear curve. The limit of detection determined from the intersection of the two extrapolated segments of the calibration graph [31] was found to be $1 \times 10^{-6}$ M, and thus the working concentration range is found to be $1 \times 10^{-1}$ M to $1 \times 10^{-6}$ M (Fig. 4) for $Mn^{2+}$ ions with a Nerstian slope of 39.00 mV per decade change in $Mn^{2+}$ ion concentration. The slope value is high to Nerstian value, 29.6 mV per concentration decade for divalent cation [32].

pH effect on the potential response of the electrode were measured for a fixed ($1 \times 10^{-2}$ M) concentration of $Mn^{2+}$ ions in different pH values. It is clear that electrode potential remains unchanged within the pH range 3.0–8.0 (Fig. 5), known as working pH for this electrode.

Another important factor is the promptness of the response of the ion-selective electrode. The average response time is defined [33] as the time required for the electrode to reach a stable potential. It is clear that the response time of the membrane sensor is found to be ~40 s (Fig. 6).

The membrane could be successfully used for up to four months without any notable drift in potential during which

period the potential slope is reproducible within $\pm 1$ mV per concentration decade. Whenever a drift in the potential is observed, the membrane is re-equilibrated with 0.1 M $Mn(NO_3)_2$ solutions for 3–4 days.

The selectivity coefficients, $K_{Mn.M}^{POT}$ of various differing cations for the Mn(II) ion selective polypyrrole Sn(IV) phosphate composite membrane electrode were determined by the mixed solution method [34]. The selectivity coefficient indicates the extent to which a foreign ion ($M^{n+}$) interferes with the response of the electrode towards its primary ions ($Mn^{2+}$). By examine the selectivity coefficient data given in Table 6, it is

**Table 6** The selectivity coefficients $\left(K_{Mn.M}^{POT}\right)$ of various interfering cations ($M^{n+}$).

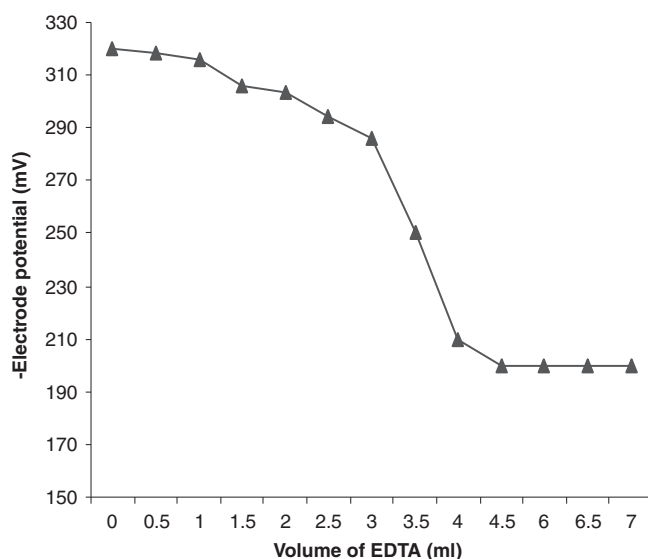| Metal ions | Selectivity coefficient values |
|---|---|
| $Na^+$ | 0.001 |
| $Mg^{2+}$ | 0.002 |
| $Sr^{2+}$ | 0.005 |
| $Al^{3+}$ | 0.008 |
| $Zn^{2+}$ | 0.009 |
| $Hg^{2+}$ | 0.007 |
| $Pb^{2+}$ | 0.006 |
| $Cu^{2+}$ | 0.001 |
| $Fe^{3+}$ | 0.005 |
| $Ca^{2+}$ | 0.003 |
| $K^+$ | 0.007 |

**Fig. 7** Potentiometric titration of Mn(II) against EDTA solution using polypyrrole Sn(IV) phosphate PVC membrane electrode.

clear that the electrode is selective for Mn(II) in the presence of interfering cations.

The practical utility of the proposed membrane sensor assembly was tested by its use as an indicator electrode in the potentiometric titrations of Mn(II) with EDTA. The addition of EDTA causes a decrease in potential as a result of the decrease in the free Mn(II) ions concentration due to its complexation with EDTA (Fig. 7). The amount of Mn(II) ions in solution can be accurately determined from the resulting neat titration curve providing a sharp rise in the titration curve at the equivalence points.

## Conclusion

In the present study, a manganese selective composite cation-exchanger polypyrrole Sn(IV) phosphate, having good ion-exchange capacity (1.04 meq/g) as compared to Sn(IV) phosphate (0.72 meq/g), has been prepared successfully. This composite material was also utilized as an electro-active component for the preparation of ion-selective membrane electrodes for the determination of Mn(II) ions in aqueous solution. The membrane electrode showed a working concentration range of $10^{-1}$–$10^{-6}$ M, response time of 40 s, 4–8 pH range, and selectivity in the presence of other metal ions. The practical utility was determined as potentiometric sensor for the titration of Mn(II) using ethylenediaminetetraacetic acid (EDTA) as a titrant.

## Acknowledgements

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