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Voltammetric Determination of Fluoride Ion Using Galvanostaticaly Grown Poly(3-hexylthiophene) Film

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Abstract: Poly (3-hexylthiohene) films have been prepared by galvanostatic technique on platinum surface. The structure and surface morphology of the film was characterized by cyclic voltammetry (CV), FTIR and SEM imaging. Cyclic voltamogram of poly (3-HTh) film showed only one reduction peak at potential 0.82 V. Cyclic voltammogram of the poly (3-HTh) film when recorded in fluoride ion solution showed two redox pair at $E_{1/2}$ = 0.048 V (A/A') and $E_{1/2}$= 0.074 V (B/B'). The former peak may be attributed to $[BF_4]^-/[BF_4]^{2-}$ redox couple and later peak to the presence of loosely bound fluoro-borate anions in the polymeric film respectively. Diffusion controlled process may be the possible reaction mechanism. The diffusion coefficient (D) and rate of reaction (*R*) for the reaction (B/B') are calculated as 9.29 × 10^{-3} cm^2 s^{-1} and 5.61 × 10^{-9} mol s^{-1} respectively. Poly (3-HTh) films showed detection limit as low as 2.5 mM. *Copyright © 2012 IFSA.*

Keywords: Polythiophene, Fluoride estimation, Galvanostatic technique, Cyclic voltammetry.

1. Introduction

According to WHO [1] fluoride ion (F^-) concentration less than 1.5 mgL^{-1} in drinking water is beneficial to health and concentration above this limit causes serious health hazards especially dental, skeletal and non-skeletal fluorosis [2]. McCollum and coworkers in 1925 [3] reported that teeth structure has direct linkage with the quantity of fluoride in drinking water. Available literature also shows a close correlation between fluoride exposure and chromosome damage in humans [4-5].

Natural sources of fluoride compounds in environment are leaching process of ores containing fluoride, emission from coal power plants in the form of gases, and from various industrial processes producing fluoride as industrial waste. According to the report of Nawalakhe and Paramasivam, [6] several states of India are affected by fluoride contamination in water.

Though, there are several methods available for the estimation of fluoride viz., titrimetry [7], spectrophotometric [8], gas chromatograph [9], ion selective electrodes [10], etc. H. Miyaji et al. have described the detection of fluoride along with other halogen family members by addition of specific reagents [11]. These ion specific electrodes can be used for detection of low concentration of fluoride ion but the electrodes get poisoned for higher concentration detection. Moreover, these methods suffer many limitations like high cost, limited shelf life, time consuming, labor intensive, and operator specific.

The present work is an attempt to demonstrate for the first time determination of aqueous solutions of specific ion (Fluoride) in mM concentration with-out the addition of any supporting electrolyte using poly-hexylthiophene as sensing material. Regioregular poly (3-alkylthiophene)s are very promising among the conductive polymers due to their high electrical conductivity and their large number of possible chemical variants. Also, poly (3-alkylthiophene)s possess environmental stability, low oxidation potential and low band gap. Presence of long alkane chains to a thiophene ring leads to the improvement in properties like solubility, and possibility [12]. These chains also lead to increased electro activity of the polymer and thereby enabling the use of such conducting polymer for detection of different ions [13]. In last decade, poly (3-hexylthiophene) has found immense applications in solar cells, biosensors, device fabrication, etc, [14-17]. Li et al., [18] used multiple regioregular polythiophene polymers as active sensing layers in a single chip chemresistor sensor array device. A custom inkjet system was used to selectively deposit the polymers onto the array of transduction electrodes. The sensor demonstrated sensitivity and selectivity for detection and discrimination of volatile organic compounds (VOCs). Pandey et al. [19] used poly(3-cyclohexylthiophene) for developing solid state pH sensor for application in urea biosensor.

Electrochemical sensing (ES) techniques are playing a growing part in various fields in which an accurate, low cost, fast and online measuring system is required. Electrochemical sensors have improved the performance of the conventional analytical tools, have eliminated slow preparation and the use of expensive reagents, and have provided low cost analytical tools. Beside the relatively low cost compared with optical instrumentation, advantages such as the possibility of miniaturization as well as in-field applications make ES devices very attractive in several fields such as environmental monitoring, food quality control and clinical analysis.

Keeping in view the advantages of electrochemical sensing, we have attempted determination of fluoride ion electrochemically using polyhexylthiophene films as sensing material. Polyhexylthiophene films were electropolymerized using galvanostatic mode. To the best of our knowledge, polyhexylthiophene has not yet been used for fluoride ion detection employing voltammetric technique.

2. Experimental

2.1. Reagents

All chemical were used as received, without any further purification: 3-hexylthiophene (3-HTh) (Spectrochem Pvt. Ltd), Tetrabutylammonium-tetrafluoroborate (TBATB), and potassium fluoride (Loba chemie). Doubly distilled water obtained from Elga PureLab ultra water purification system was used in all the experiments.

2.2. Instrument

The electrochemical studies were carried out using Solartron 1285 PSTAT/GSTAT in an electrolytic cell having single compartment with three electrodes: reference (saturated calomel electrode, SCE), counter (platinum foil, 25 mm^2) and working (platinum disc electrode of 2 mm diameter, from CH instruments, Inc.) electrode. Fourier Transform Infra-Red (FTIR) analysis was performed on Perkin Elmer Spectrum RX/FTIR system. JEOL JSM 6100 was used for SEM studies.

2.3. Preparation of Modified Electrode

Before deposition, the platinum working electrode was activated by polishing with fine grade aqueous alumina slurry (grain size 1, 0.3 and 0.05 μm in a sequence) on a polishing cloth and then rinsed thoroughly with double distilled water. Poly (3-hexylthiophene) film was deposited to platinum disc electrode of diameter 0.2 cm by galvanostatic technique at a current density of 5 mA cm^{-2}. The electrolyte solution consisted of 0.1 M 3-HTh monomer and 0.1 M TBATB as a supporting electrolyte and nitrobenzene (10 ml) as solvent. All electrochemical studies were carried out at 25 ± 1 °C temperature. Once prepared, poly (3-HTh)/Pt electrode was taken out from the solution and washed thoroughly with nitrobenzene to remove monomer (if present). This modified electrode was used as a working electrode in cyclic voltammetry experiments to study the redox behaviour of the film in KF solution in the potential range from -1.2 to 1.2 V at (10-50) mVs^{-1} scan rate. A fresh electrode was employed every time for study as movements of ions into and out of the film may alter the composition of modified electrode. For FTIR and SEM imaging, the poly (3-HTh) film was electrochemically deposited on an indium tin oxide (ITO)-coated glass electrode under similar conditions.

3. Results and Discussion

3.1. Electrochemical Polymerization of pt/poly (3-HTh)

The electrochemical formation of conducting polymers is a unique process. Although it represents some similarities with the electrodeposition of metals since it proceeds via a nucleation followed by phase growth mechanism [20-21], the major difference lies in the fact that the charged species precursors of the deposited materials must be initially produced by oxidation of the neutral monomer at anode surface. The consequence of this is that various electrochemical and chemical follow-up reactions are possible [22]. Polymerization has been carried out at different applied currents from 1 to 10 mA. Polymerization is achieved at a very fast rate i.e. within 10 s for 10 mA applied current. It has been further observed that at 5 mA applied current, potential increased with time up to 35 s thereafter reaches a constant value of 2.4 V. The polymerization is actually achieved within 35 s but the run is continued for 60 s in order to ensure that maximum possible polymerization could take place. At this point of polymerization, platinum disc electrode is fully covered with the polymeric film and hence no further change in potential is observed. Slow rate of polymerization ensures formation of compact and uniform film, thus in the present study we have used polymer films prepared at applied current of 5mA. However, at current value below 5mA (1-4 mA), polymerization was very slow but films obtained were not uniform. The surface coverage (τ) of poly (3-HTh) film deposited was estimated to be 4.13×10^{-5} mol cm^{-2} using eq. (1) based on Faraday's first law:

$$\tau = Q/nFA \quad (1)$$

where, Q is the charge passed; n is the stoichiometric number of electrons consumed, A is the electrode area and F is Faraday's constant.

3.2. FTIR study of poly (3-HTh)

The infrared spectrum of poly (3-HTh) is shown in Fig. 1. In the 2800-3100 cm^{-1} region, carbon-hydrogen stretching fundamental modes are expected in the infrared spectra. The band observed at 2961 cm^{-1} is assigned to methylene groups in the hexyl chain. At 1473 cm^{-1}, CH_3 and CH_2 bending are observed. Bands observed at 637 and 1339 cm^{-1} are assigned to hexyl group.

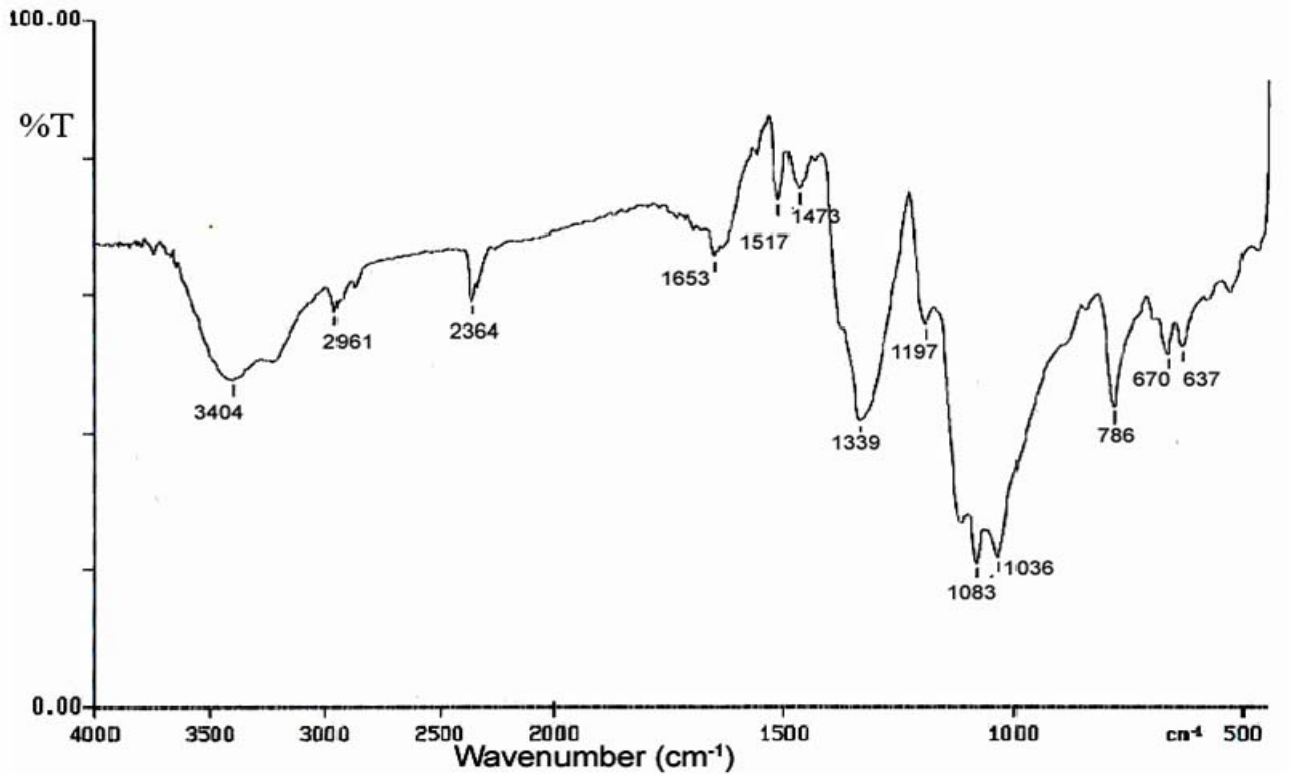

Fig. 1. FTIR spectrum of Pt/poly (3-HTh).

The strong intensity of the 786 cm^{-1} band which is characteristic of 2,5-disubstituted thiophene rings indicates that the electrochemical coupling of thiophene ring occurs preferentially at 2,5 positions [23]. Table 1 describes all the absorption peaks observed in the FTIR spectrum.

Table 1. Observed peaks in FTIR spectrum of poly(3HTh).

Types of vibration	Peak frequencies (cm^{-1})	Approximate description of vibrations
Alkyl modes (hexyl group)	2961	C-H stretching, anti-symmetric
	2364	C-H stretching, symmetric
Ring skeleton in plane (thiophene ring)	1653	C=C stretching, anti-symmetric
	1517	stretching of C=C outside of phase
	1473	asymmetric (CH_3), CH_2 scissor
	1339	C-H bending in plane
	1197, 1083, 1036	Deformation band of C–H in-plane of thiophene, Doping of polymer
Ring out of plane deformation	786	C-S-C deformation (2,5-disubstituted thiophene ring)
	670,637	S-C stretching

3.3. Scanning Electron Microscopy (SEM)

The SEM micrograph (Fig. 2) of poly (3-HTh) film showed porous morphology with pores of size ~1.5µm. Porosity of film enhances the interaction at the interface and facilitates unobstructed movement of fluoroborate ions at the surface.

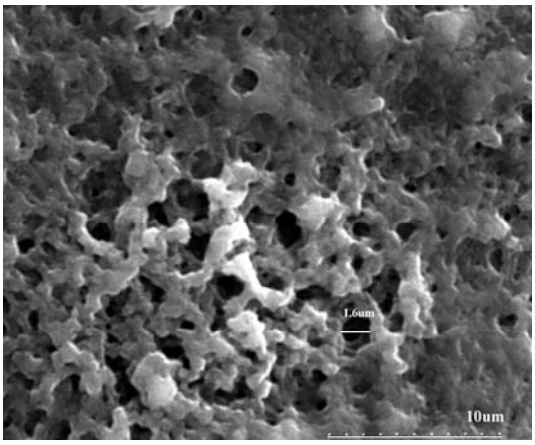

Fig. 2. SEM image of electrochemically polymerized poly (3-HTh).

3.4. Electrochemical Studies of Poly (3-HTh)

3.4.1. Cyclic Voltammogram Studies

CV study of bare platinum and pt/poly (3-HTh) was carried out in a solution containing supporting electrolyte, TBATB (0.1 M) in nitrobenzene (Fig. 3).

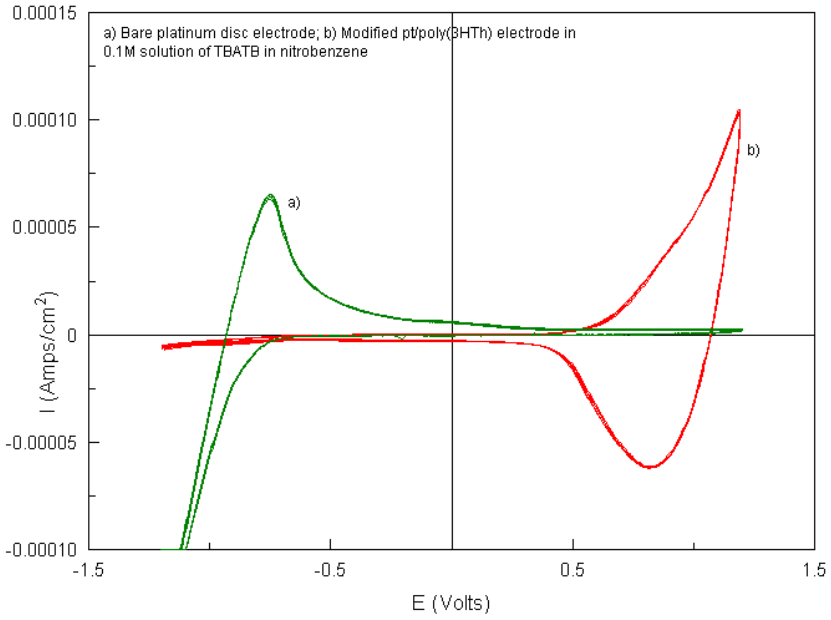

Fig. 3. Cyclic voltammogram of (a) bare platinum and (b) Pt/poly (3-HTh) in nitrobenzene containing 0.1 M TBATB.

The appearance of the oxidation peak at E = -0.75 V can be attributed to the process of oxygen reduction at bare platinum electrode [24-25]. The CV spectrum for pt/poly (3-HTh) in the same solution gave a single reduction peak at potential value of 0.82 V which can be endorsed to the reduction of polymer film in presence of TBATB. Also, the complete disappearance of peak at E = -0.75 V indicates that the platinum disc is completely covered with the polymer film.

3.4.2. Cyclic Voltammetry behavior of pt/poly (3-HTh) Electrode in KF Solution

Pt/poly (3-HTh) electrodes have been explored for application in fluoride estimation using cyclic voltammetry. The cyclic voltammogram of Pt/poly (3-HTh) was recorded in KF solution and deionised water within the potential range -1.2 to +1.2 V Vs Standard Calomel Electrode (Fig. 4) at scan rate of 50 mV/s. For KF solution, no additional supporting electrolyte was added during cyclic voltammetry as it is a strong electrolyte and ensures high ionic strength [26].

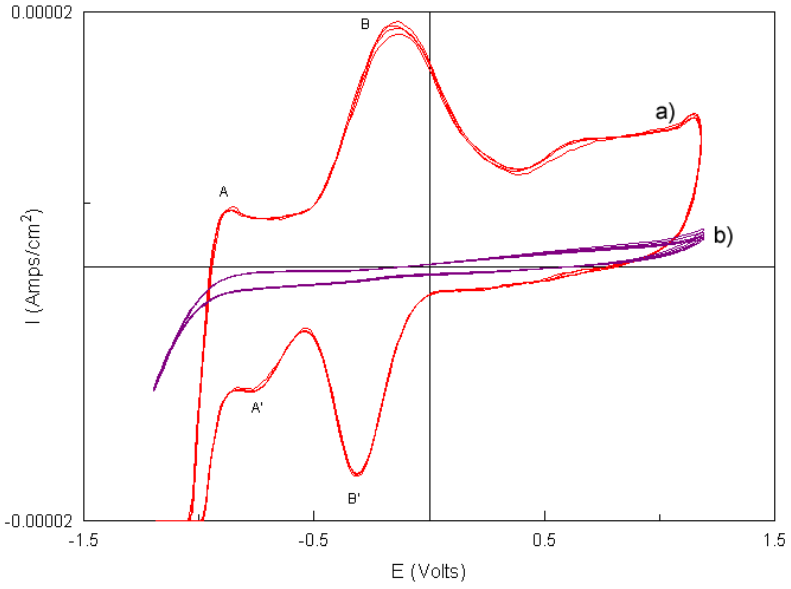

Fig. 4. CV spectra of Pt/poly (3-HTh) recorded in (a) KF solution, (b) in deionized water.

The spectrum shows two distinct redox pair at $E_{1/2}$ = 0.048 (A/A') and $E_{1/2}$= 0.074 V (B/B'), which suggests the existence of two types of redox reactions. It can be hypothesized from the observations that B/B' redox pair appears due to loosely held electrons which are prone to easy removal from the polymer matrix (Fig. 5a). Thus B/B' redox pair may be attributed to the oxidation reduction of the polymer film due to the movement of dopant ion in the presence of strong electrolyte solution of KF. The appearance of A/A' redox pair might be due to the occurrence of $[BF_4]^-/[BF_4]^{2-}$ in the electrolyte solution (Fig. 5b). The oxidation process (or doping) of the polymer (from -1.2 to 1.2 V) corresponds to the transfer of dopant ions (fluoro-borate ion) from polymer surface to electrolyte solution, producing holes. Meanwhile, anions (fluoride ions) diffuse into the polymer and form anion-hole pairs to maintain electro-neutrality. In reverse sweep (reduction or de-doping), the anions (F^-) are expulsed towards the electrolyte accompanied by a reorganization process of the polymer chains.

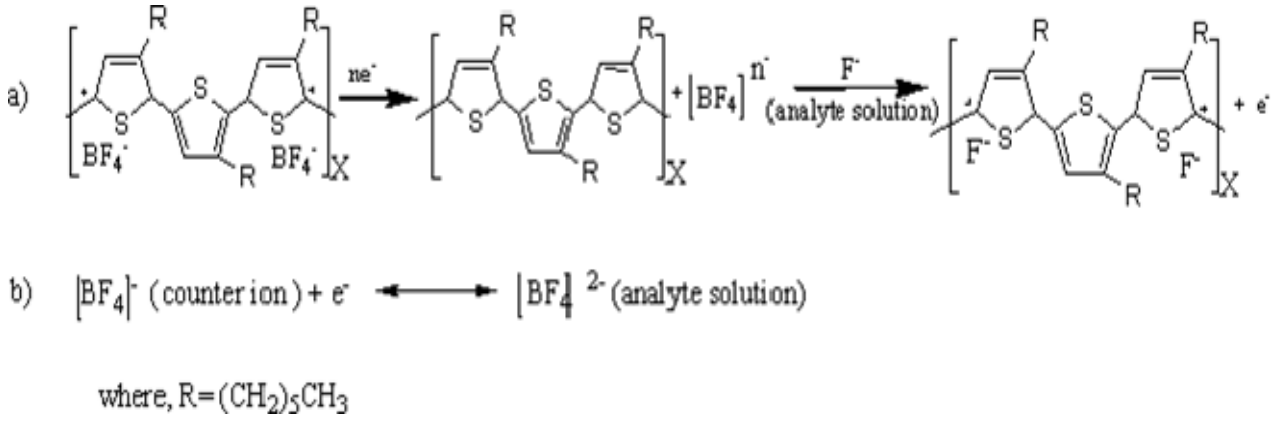

Fig. 5. Stepwise presentation of possible reduction-oxidation of film at the interface of film surface and solution (a, b)

Anodic to cathodic peak separation (formal potential, $\Delta E = E_{pa} - E_{pc}$) at pt/(3-HTh) electrode for the redox pair A/A' and B/B' are 116 and 94 mV respectively. The redox processes A/A' and B/B' are quasi-reversible as $\Delta E > 59$ mV however, the process B/B' appears to be more reversible. As calculated from the expression, $n=0.059/\Delta E$, it has been observed that approximately 0.3 (A/A') and 0.6 (B/B') electron transfer process is occurring. The ratio of oxidation to reduction peak currents (I_{pa}/I_{pc}) for B/B' redox pair is 1.15 which indicates reasonably fast electron transfer kinetics at all scan rates investigated. The (I_{pa}/I_{pc}) is 0.5 for A/A' which indicates that $[BF_4]^-/[BF_4]^{2-}$ redox couple (Fig. 5b) is a comparatively slow reaction. The rate of the reaction (R) has been calculated to be 1.45×10^{-9} and 5.61×10^{-9} mol s^{-1} respectively for the reactions A/A' and B/B' using equation 2.

$$R \text{ (mol s}^{-1}) = i/(nFA) \quad (2)$$

where, n is the stoichiometric number of electrons consumed, A is the electrode area and i is the current and F is Faraday's constant.

3.4.2. Study as a Function of Fluoride Ion Concentration

CV of pt/poly (3-HTh) has also been recorded as a function of KF concentration and scan rate. As a function of KF concentration (0.0025-0.1 M), anodic peak current increased with no shift in peak position i.e. I_{pa} is directly proportional to KF concentration (Fig. 6).

Fig. 6B shows the amperometric response of KF concentration as a function of anodic peak current density (i). A linear plot with correlation coefficient ($R^2 = 0.986$) illustrates satisfactory results for the determination of fluoride ion concentration in the studied range. As manifested by the plot, the sensitivity of the reaction is ~18.5×10^{-5} $Acm^{-2}M$. It has been further observed that with an increase of 95 % in concentration there is 67% increase in current density value.

3.4.3. Study as a Function of Scan Rate

At the same time, current variation was also studied as a function of scan rate in 0.05 M KF solution. There is a substantial increase in the peak current density (I_{pa}) at B with square root of scan rate ($S^{1/2}$) (Fig. 7), thus showing a quasi-reversible reaction taking place.

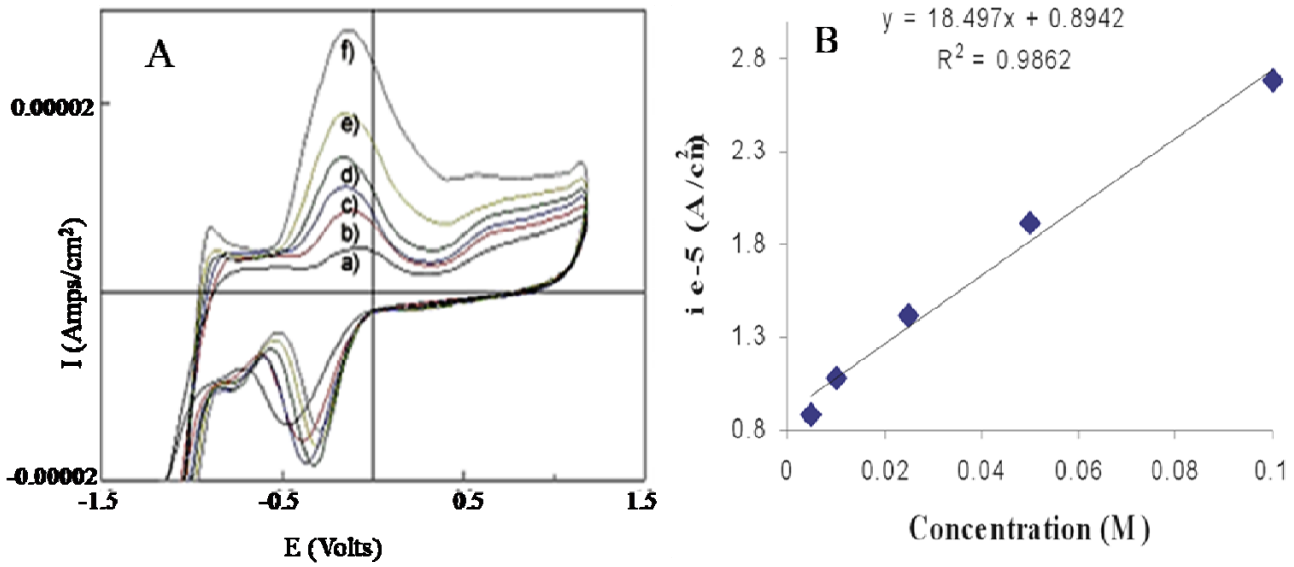

Fig. 6. A) CV of Pt/poly (3-HTh) as a function of KF concentrations (a) 0.1 M, (b) 0.05 M, (c) 0.025M, (d) 0.01 M (e) 0.005 M (f) 0.0025 M; B) Amperometric response of Pt/poly (3-HTh) electrode as a function of KF concentration.

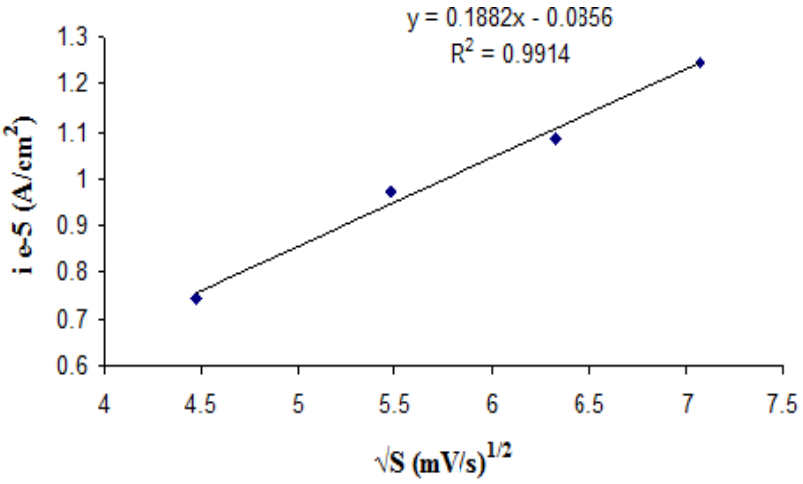

Fig. 7. Plot of oxidation peak current density (I_{pa}) Vs square root of scan rate (√S).

Linear equation of plot indicates the dominance of diffusion controlled process with correlation co-efficient (R^2) of 0.991. Diffusion coefficient as calculated from the plot between charge (Q) and square root of scan rate (√S) comes out to be 9.29×10^{-3} cm^2 s^{-1}. A further study is underway regarding ways of improving detection limit and the possible application of the sensor in the detection of fluoride ion in water.

4. Conclusion

Poly (3-hexylthiophene) film has been successfully synthesized on platinum surface using galvanostatic technique at a current rate of 5 mA/cm^2. Cyclic voltammograms of the resulting polymer film indicates the presence of quasi-reversible redox pair. The film prepared has been characterized by FTIR, SEM study and electrochemical analysis. The high electroactivity of poly (3-HTh) film due to porous morphology and free ions on the surface of the film enables it to act as a potential polymeric

material for sensor application. The cyclic voltammetry study of the film in potassium fluoride solution shows two distinct redox pairs. A possible stepwise mechanism has been proposed for the movement of ions and electrons at the interface of film and electrolyte solution. The lower detection limit of the film for potassium fluoride has been obtained to be 2.5 mM.

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