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# $Fe^{3+}$ ion sensing characteristics of polydiphenylamine—electrochemical and spectroelectrochemical analysis

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## Abstract

Polydiphenylamine (PDPA) film was deposited on platinum/indium tin oxide coated glass (ITO) electrode in aqueous acidic medium and analyzed for the changes in redox characteristics in the presence of acidified iron (III) chloride ($FeCl_3$). PDPA seems to capture $Fe^{3+}$ ions and further transforms into $Fe^{2+}$ ions through interaction with its redox binding sites, as confirmed through results from cyclic voltammetry and UV–vis spectroscopic studies. The redox behavior for the PDPA film modified with $Fe^{3+}$ ions was evaluated through in situ UV–vis spectroelectrochemical studies. In situ studies demonstrate that PDPA is partially reduced in the presence of $Fe^{3+}$ ions and the redox transformation was almost reversible. Modified PDPA film electrode showed Nernstian potential response for $Fe^{3+}/Fe^{2+}$ redox process and such modification is expected to be suitable for sensor applications.

*Keywords:* Polydiphenylamine; Ferric ion; Redox interaction; Sensor

## 1. Introduction

Conducting polymers find increasing usage in various branches of technology, such as metallization of dielectrics, primary and secondary batteries, antistatic coatings, electromagnetic shielding, electrochromic systems, etc. [1–3]. Conducting polymers have also been utilized as an effective matrix for chemical sensors [4] and pH sensors [5,6]. The properties of the conducting polymers can be modified by attaching functional groups or by the incorporation of different counter ions in their backbone. The fact that the molecular structure of conducting polymers has a profound influence on their electrical and electronic properties enables interactions of the groups present in the conducting polymer with other chemical species and this forms the basis of sensor applications. It is a proper selection of conducting polymer to sense the chemical species of interest is to be made, the interaction aspects between them should be understood in the process of making sensor. A feasibility study on the interaction of a conducting polymer with certain analytes or group of analytes has been reported [7].

Among the conducting polymers, polyaniline (PANI) has been widely studied as sensing materials [4,5]. Moreover, the PANI–metal ions interactions are more pronounced by the presence of a functional group attached on the benzene ring such as hydroxyl [5,6] or amine [8]. It has been reported that among the PANI derivatives, poly(*N*-*N*-dimethylaniline), and poly(*N*,*N*-*n*-dibutylaniline) have anion exchange ability because of the presence of positively charged quaternary ammonium nitrogen in the polymeric chain. The anion exchange ability is useful in anion sensor applications. A novel complex catalyst system for dehydrogenation of few amine derivatives consisting of palladium (II) acetate and PANI has been established [9].

Recently, research activities are directed on polymer of few *N*-substituted aniline derivatives. Polydiphenylamine (PDPA), *N*-aryl substituted aniline, is found to show many properties that are different from PANI and other *N*-substituted aniline derivatives [10–12]. An amperometric sensor involving PDPA has been reported for simultaneous determination of electro-inactive anions and cations such as $SO_4{}^{2-}$, $Cl^-$, $NO_3{}^-$, $Na^+$, $NH_4{}^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ as a detector in ion chromatography [13]. An amperometric detector with working electrodes modified with polydiphenylamine-dodecyl sulfate (PDPA-DS) was

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successfully used for the simultaneous determination of electro-inactive anions ($SO_4^{2-}$, $Cl^-$, $NO_3^-$) and cations ($Na^+$, $NH_4^+$ and $K^+$) in single-column ion-exclusion cation-exchange chromatography (IEC-CEC). The working electrode was stable over one week period of operation with no evidence of chemical and mechanical deterioration [14].

The use of PDPA as sorbent for the solid-phase extraction of some phenolic compounds from water has been reported [15]. The utility of PDPA as sensor for aliphatic alcohols such as methanol, ethanol, propanol, butanol and heptanol has been demonstrated [16]. PDPA exhibits electrochromism as a layer in flexible electrochromic display devices [17]. These devices exhibit great contrast in the visible/near infrared (IR) spectral region with high reflectance in their reflecting state, due to morphological changes induced by the movements of ions in the polymer films, is measured by EQCM with fast simultaneous acquisition of frequency and impedance. Highly conducting films of polydiphenylamine-$BF_4^-$ anion (PDPA-$BF_4$) were synthesized in neutral and acid non-aqueous media electrochemically modified by iodide species in $HClO_4$ aqueous media containing $I^-$ ions [18]. Soluble conducting polydiphenylamine doped with methane sulphonic acid have been reported [19].

Recently, Gopalan and co-workers [20] have established the utility of PDPA and its copolymer films for tuning pH sensitivity close to 7 and revealed the possibility of using in biosensor applications. The pH sensitivity, reproducibility and response time were evaluated and compared with that of PANI. To our knowledge, a systematic study on understanding the interaction of PDPA with metal ions has not been performed so far. Also, reports using in situ UV–vis spectroscopy as a tool to evaluate the redox behavior of the conducting polymers in the presence of metal ions are scarce.

The present study aims to understand the molecular interactions between functional groups in PDPA and ferric ions to evaluate the possible use in sensor applications. It was envisaged that the presence of ferric ions in the PDPA environment would alter the redox characteristics of PDPA. Hence, systematic electrochemical and in situ UV–vis spectroelectrochemical studies were carried out on PDPA modified electrodes under different conditions of $FeCl_3$/1 M HCl solutions.

## 2. Experimental

### 2.1. Preparation of PDPA/PDPA-Fe film

Film of PDPA was deposited on platinum/indium tin oxide coated glass (ITO) electrode by electropolymerization of DPA with a concentration of 40 mM in 4 M $H_2SO_4$ by cyclic voltammetry and cycling the potential in the range of 0.0–0.8 V. Films of PDPA on Pt or ITO electrodes were subjected to oxidation and reduction in 1.2 mM $FeCl_3$/1 M HCl solutions for 5 cycles, rinsed several times with doubly deionized water and stored in oxygen free environment. These films were referred to as Pt/PDPA-Fe or ITO/PDPA-Fe films.

### 2.2. Measurements

#### 2.2.1. Electrochemical measurements

Electrochemical experiments were carried out in a three-electrode cell assembly. A platinum disc electrode of area 0.25 $cm^2$ was used as working electrode. A platinum wire and SCE were used as the counter electrode and the reference electrode, respectively. CVs were recorded by using Bio Analytical System (BAS 100BW). PDPA films were kept in 1 M HCl or in a solution of $FeCl_3$ in 1 M HCl and CVs were recorded. CVs of the stabilized (as indicated from the constancy of CV pattern) films were considered for discussion.

#### 2.2.2. UV–vis spectroscopy

UV–vis spectrum of the PDPA/PDPA-Fe film on ITO coated glass plate were recorded by using Shimadzu UV-2401 PC spectrophotometer.

#### 2.2.3. In situ UV–vis spectroelectrochemical measurements

In situ UV–vis spectroelectrochemical experiments were performed on ITO/PDPA-Fe electrodes by placing the polymer coated ITO glass plate (with a specific surface resistance of about 10 Ω/□) in the quartz cuvette of 1 cm path length perpendicular to the light path. Spectroelectrochemical cell was assembled. A platinum wire was used as counter electrode and Ag/AgCl was used as reference electrode. Before each experiment, the ITO coated electrode were degreased with acetone and rinsed with an excess of distilled water. Spectroelectrochemical data were collected by recoding the CV of the ITO/PDPA or ITO/PDPA-Fe electrode by sweeping the potential between 0.0 and 0.8 V with a slow scan rate and simultaneously recoding the UV–vis spectra. Also, the potential of the ITO/PDPA or ITO/PDPA-Fe electrode was kept constant for 5 min and the UV–vis spectrum was recorded while holding the potential. A quartz cuvette containing an ITO coated electrode glass plate without having any polymer coating was used as reference.

## 3. Results and discussion

### 3.1. Electrochemical behavior of PDPA film

Fig. 1(i) (solid lines) represents the CV of PDPA film on a platinum electrode in 1 M HCl and the redox characteristics are assigned. PDPA shows two distinguishable redox pairs in the potential range 0.0 and 1.0 V. These two peaks are assigned to the generation of *N*,*N*′-diphenyl benzidine type radical cation ($DPB^+$, polaronic form of PDPA) and *N*,*N*′-diphenyl benzidine dication ($DPB^{2+}$, bipolaronic form of PDPA). Otherwise, the reduced PDPA is oxidized