

SINI VARGHESE C. “ EVALUATION ON THE INHIBITIVE EFFECT OF HETEROCYCLIC DERIVATIVES AND POLYAMINO COMPOUNDS ON THE CORROSION OF CARBON STEEL AND COPPER IN ACID MEDIA.” THESIS. RESEARCH AND POSTGRADUATE DEPARTMENT OF CHEMISTRY, ST. THOMAS’ COLLEGE (AUTONOMOUS), UNIVERSITY OF CALICUT, 2019.

## **PART III**

# **CORROSION INHIBITION BY PROTECTIVE COATINGS**

# CHAPTER 1

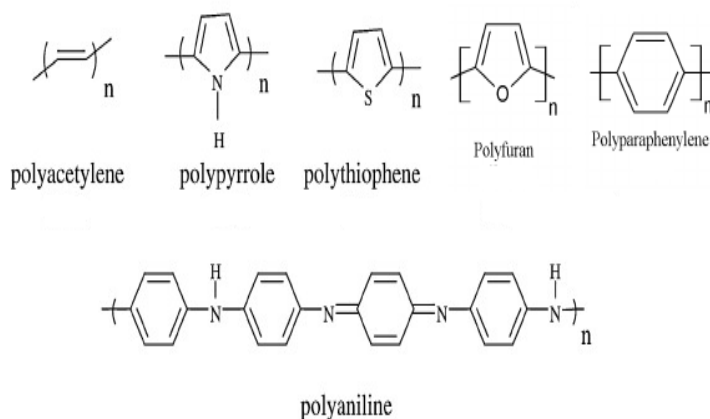
## INTRODUCTION AND REVIEW

Economic inflation and catastrophic effect occurs due to corrosion. To minimize the corrosion, scientists and researchers are ever in searching for novel and effective methods. Out of various methods to combat against corrosion is to make protective coatings on the metallic substrates. To find out an effective, durable and protective coating is a thrust area of research in the field of corrosion protection. Apart from the conventional coatings using paints, oils, varnishes etc, nowadays scientist rely upon special type of polymeric coatings. To reduce metallic corrosion, chromate coatings have been widely used in metal industries for a long time. Chromate coatings mainly inhibit the anodic process of corrosion<sup>1-7</sup>. Serious disadvantages of chromate coating are their toxicity and difficulty in handling<sup>8,9</sup>. At present these coatings are replaced by rare earth metal or metal oxide as well as organic polymeric coatings.

Apart from the inorganic coatings, organic polymer coatings have many advantages such as improved chemical resistance, good thermal stability, high corrosion protection efficiency, better surface shine and appreciable electric as well as magnetic properties<sup>10-19</sup>.

In earlier days organic polymeric coatings were done by chemical synthesis. Nowadays polymeric anticorrosive coatings are mainly done by electrochemical methods. Electro deposition is the most convenient way to make protective coatings using conducting polymers. It can be performed under potentiostatic or cyclic voltammetric conditions.

Corrosion scientists have been focused in the research of conducting polymeric coating for many years<sup>20-26</sup>. Conducting polymers play a significant role in corrosion protection in two ways. Primarily they act as a physical barrier against corrosion. Secondly they will protect the metal surface by making a suitable electronic barrier<sup>27</sup>. Conducting polymers are able to oxidize the metal surface and make passive oxides. This allows shifting the potential of the coated metal more towards cathodic side and hence metal will be protected<sup>28,29</sup>. Familiar examples for Intrinsically Conducting Polymers (ICP) are Polyacetylene, Polypyrrole, Polythiophene, Polyfuran, Polyaniline and Poly para-phenylene as given in the Figure.

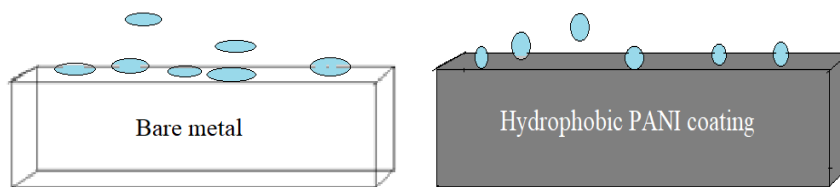


#### Intrinsically Conducting Polymers (ICP)

The protective capacity of simple top coat systems and primer top coats containing inorganic corrosion inhibitors are less, compared to the combination systems involving conducting polymers. Many industries rely upon these combined top coat system containing epoxy and/or polyurethane resins and conducting polymers which display better corrosion protection against corrosive media<sup>30-32</sup>. Suitable blending of the conducting polymers and the above

mentioned resins would render enhanced corrosion protection than the simple polymeric coatings<sup>33</sup>.

Several strategies were employed by scientists and technologists for the applications of conducting polymers as protective coatings. Conducting polymers can be electrodeposited easily on the surface of the metals and hence they will act as primers on the metal surface<sup>34,35</sup>. Some researchers have noticed the high corrosion protective efficiency of conductive polymers when they are blended with conventional top coat resins like epoxy, polyurethane etc and applied on the metal surface<sup>36</sup>. Conducting polymers can be substituted for inorganic anticorrosive materials used in paints. As a result, corrosion preventing capacity of coating of paint can be improved very much<sup>37</sup>. Hydrophobic conducting polymer coating offers better corrosion prevention by repelling the water droplets from their surface as shown in the Figure given below.



Corrosion protection of polymer coating due to hydrophobic nature

## Methods of polymerization

### Electrochemical method

Conjugated polymers can be synthesized using electrochemical polymerization. Polypyrrole, polyacetylene, polyaniline etc are examples for the conventionally synthesized conducting polymers using electrochemical methods. The electrochemical polymerization is usually carried out on a conductive

substrate (metal or carbon electrode). The synthesized polymeric coating on the electrode surface will be in the oxidized state (conductive form). The main advantage of this technique is that we can directly dope the polymers with various anions and the level of doping can be easily adjusted. Potentiostatic or cyclic voltammetric methods are the commonly used electrochemical techniques. Anodic oxidation of the monomer leads to the formation of a radical cation which subsequently reacts with another monomer to form dimer and finally polymer. The main advantage of the cyclic voltammetry is that we can characterize the synthesized polymeric material during the electrochemical reaction. By adjusting the number of cycles in cyclic voltammetry one can change the thickness of the coated polymer on a conductive electrode.

### **Chemical method**

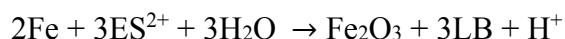
Chemical polymerization is a very popular method for the synthesis of conducting polymers. The only difference between the chemical and electrochemical method is the use of an oxidizing agent instead of electrode. Firstly the monomer is dissolved in a suitable solvent and the oxidant is added slowly at low temperature. The monomer will convert into a radical cation and it will further react with another monomer and finally a polymeric chain is formed. Ammonium persulphate, potassium permanganate, potassium dichromate, hydrogen peroxide etc are the commonly used oxidants. Since the solubility of conducting polymers are low they will be precipitated out from the solution. In actual practice it is difficult to make a polymeric coating on the surface of a substrate after the synthesis. For this purpose, the substrate surface is firstly

enriched with oxidant/monomer followed by the reaction with monomer/oxidant. This method provides convenient way to make a local coating on the surface of a substrate.

### **Review on corrosion inhibition by protective coatings**

Nicho et. al., reported the electrochemical synthesis of Polyaniline (PANI) thin films using cyclic voltammetry on stainless steel. The steel was previously covered with a thin film of polyvinyl acetate. Polarization studies have been employed for the investigation of the corrosion resistance in 0.5M H<sub>2</sub>SO<sub>4</sub> and 0.5M NaCl. Authors claim that PANI-PVAc coatings showed good protection efficacy than the uncoated samples in these media. Compared to the simple PANI films, the PANI-PVAc showed better performance<sup>38</sup>.

Many researchers have been evaluated the corrosion protection ability of the coatings in sodium chloride (NaCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and sodium hydroxide (NaOH) media. The mechanism of protection of iron by doped PANI shown that Emeraldine salt of PANI (ES) PANI and Leuco base of PANI (LB) form a redox couple which can be regarded for the establishment of the potential of iron in the passive region. The LB that has been formed is cyclically oxidized to ES again by the reduction of oxygen so that the potential of iron is always maintained in the passive region<sup>39,40</sup>. The overall mechanism for the protection of Fe can be summarized as follows



Various researchers examined the prolonged corrosion protection ability of polyaniline and other conducting polymeric coatings in acidic medium. Recently Bernard et. al., evaluated the protective character of PANI by electrodepositing the materials on iron surface from oxalic medium. They studied the capacity of PANI film to protect the acidic corrosion by treating the sample containing sulphate ions (pH= 4.5). They proved that PANI has been found to be effective for corrosion prevention during at least 10h in this medium. Surface analysis was conducted using spectroscopic techniques such as Raman spectroscopy and reflectance measurements<sup>41</sup>.

Fenalon and co-workers made efficient protective layer of polypyrrole on CuZn electrode. The deposition was achieved by the electro polymerization in sodium oxalate acid medium. This medium was very effective in making a conductive but passivating layer on the surface of CuZn electrode. First a pseudopassive layer of copper oxalate containing Zn is formed. This layer was sufficiently conducting and the polypyrrole was electropolymerized on the electrode. The corrosion protective power of the polypyrrole film was evaluated in acidic, neutral and NaCl solutions. They reported that on immersing these electrodes in these solutions for a very long time, some of their protection properties decreased<sup>42</sup>.

Few researchers claim that the iron surface gets passivated during the electropolymerization of aniline. This passivated layer is responsible for the corrosion protection of iron. In addition to this, electrodeposited PANI film will stabilize the passivated layer<sup>43</sup>.



In 2001 S. Souza et. al., have reported the corrosion protection capacity of acrylic blend formed by camphor sulphonated doped PANI and poly(polymethyl methacrylate) on iron surface. This coating was very effective in protecting the iron surface from chloride solutions. Studies showed that this coating inhibit the corrosion of Fe surface in two ways. It makes a passivating complex with the dopant camphor sulphonate and simultaneously acting as a physical barrier to keep away the chloride ions from interacting with the Fe surface <sup>44</sup>.

A PANI coating on carbon steel was made by Amit Nautiy et. al., from two solutions. They electrodeposited the PANI films from oxalic acid and sodium salicylate solutions. It is established that a passive film was first formed on the CS surface when treated in oxalic acid and PANI was deposited on this passive film. They proved the formation of passive layer using cyclic voltammetric experiments. On decreasing the concentration of oxalic acid, the incomplete polymerization of PANI was occurred on CS surface. During the deposition of PANI from the salicylate solution voltammetric curves did not exhibit any sign of passivation. But a smooth and transparent film of PANI was deposited on the CS surface in this case. The progress of reaction, morphology and features of the coated films were studied by cyclic voltammetry, scanning electron microscopy and Raman spectroscopy<sup>45</sup>.

Kamaraj K et. al., synthesized a new polymeric coating PANI on vinyl and acrylic resin for the protection of Fe surface. In order to minimize the interaction between the dopant anion and Fe, they used benzoate anions. They proved by electronic impedance spectroscopic studies that the benzoate doped PANI acted as

a good barrier for corrosion in neutral and acidic medium. They studied the corrosion protection ability of this coating for an exposure period of 100 days<sup>46</sup>.

A novel coating on the iron surface was made by Baldissera et.al., in 2012. The specialty of this coating was the well known conducting polymer doped with various species like sulphonates, phosphates and chromates and mixed with epoxy resin. They studied the corrosion efficacy of this mixed coating materials in 3.5% NaCl medium using various electrochemical techniques. They established that on the addition of the doped PANI to the epoxy resin, enhanced the corrosion protection ability of coating<sup>47</sup>.

An extensive study on the failure of PANI films to protect the corrosion of stainless steel was done by Jianjun Fang et. al.. The film of the polymer was coated by cyclic voltammetry in 0.2M sulphuric acid medium. They proved that the corrosion protection ability of the coated polymer enhanced considerably with the thickness of coating. They claim that PANI film (emeraldine form) has an ability to oxidize the iron surface and make a passivation layer. During this process of oxidation PANI changes its behaviour slowly and it loses its corrosion protection ability. They also argue that emeraldine form get gradually reduced on the steel surface<sup>48</sup>.

The corrosion protective power of PANI doped with camphor sulphonic acid has been established by Yingjun Zhang et. al., in 2017. They mixed the doped PANI with epoxy resin and coated on mild steel surface. They also tried PANI-HF system and compared the results and proved that PANI doped with camphor sulphonic acid acted as good protective layer. The layer was analyzed

using SEM and XPS. They proved that the morphology of PANI changes appreciably when it is doped with camphor sulphonic acid<sup>49</sup>.

Ansari et. al., have been investigated the corrosion protection ability of the coating PANI (emeraldine base form) blended with nylon 66. PANI was prepared by chemical synthesis using persulphate as the oxidant. Corrosive media such as HCl and NaCl were taken and the coated samples were immersed in the same. They mainly used the half cell potential measurements and weight loss studies for monitoring the corrosion of steel. They proved that PANI-nylon coating protected well the steel surface in corrosive medium. They also found that this coating mainly prevented the anodic process of corrosion<sup>50</sup>.

Using cyclic voltammetry, conducting polymers such as poly-2-aminobenzoic acid and poly-2-chloroaniline has been synthesized very recently by Nabey et. al.. Aqueous medium of oxalic acid anion with the surfactant 'Tween 80' was used to dissolve aniline samples. The coated polymeric materials on steel surface were subjected to corrosion inhibition studies in 0.5M H<sub>2</sub>SO<sub>4</sub> using Tafel and impedance studies. Results showed that these polymeric materials acted as very good anti-corrosion film on the steel surface<sup>51</sup>.

Effect of substituents on the benzene ring of PANI was extensively studied by C. Xing et. al.. They chemically synthesized a series of polyanilines by co-polymerizing aniline with 3-aminobenzenesulfonic acid, 3-aminobenzoic acid, 3-methylaniline and 2-ethylaniline using ammonium peroxodisulphate as an oxidizing agent. Their principal aim was to incorporate hydrophilic and hydrophobic groups in the polymeric chain. They coated these microcrystalline

polymers on the steel surface and investigated their corrosion protection ability in sulphuric acid medium. They adopted polarization and EIS analytical tools for monitoring the rate of corrosion in acidic medium. According to their research, these polymeric coating mainly lowered the rate of cathodic corrosion process. They also measured the surface wettability of the polymeric chain and concluded that co-polymers which have the highest water repellency acted as good protective layer on steel surface<sup>52</sup>.

P. J. Kinlen et. al., investigated the corrosion inhibition efficacy of PANI doped with phosphonic acid and sulphonic acid. They studied the corrosion protection ability of this coating with the help of electrochemical studies and salt fog test. This experiment revealed that sulfonic acid dopants displayed an enhanced galvanic activity with time while the phosphonic acid dopants exhibited decreased activity with time, indicating passivation of the metal surface<sup>53</sup>.

### **Scope and objectives of the present investigation**

Making a protective coating using conducting polymers and co-polymers and checking their protective power towards corrosion is a fast growing research. Many researchers have tried this methodology for protecting the metals using the well known conducting polymer polyaniline (PANI). Some investigators has been made co-polymeric layer on metallic surface. When we go through the literature, it is quite clear that many of the articles related to the conducting polymeric coating are based on PANI or its co-polymer with other amino compounds or composite materials of PANI. Only very few literature are available on the polymeric coatings derived from the simple derivatives of aniline. The principal

aim of this study is to find out an effective conducting polymeric coating to protect the metallic substrate from corrosion.

The protection capacity of a polymeric sample on steel will be notable, if it shows the corrosion inhibition in the acidic medium for a long time. To determine the prolonged corrosion inhibition capacity of the polymers in aggressive medium, investigations were performed in two different ways i) after coating the steel specimens with desired polymeric materials, it was exposed to air for 24 hour and performed the electrochemical analysis in 1.0M HCl solution, ii) the coated steel specimens were directly immersed in 1.0M HCl for a period of 24 hour and conducted electrochemical experiments.

The effect of substituent on the PANI back bone may increase or decrease the conductivity and corrosion inhibition capacity of the polymeric material on steel. The present study also aims to reveal the effect of substituent on the corrosion inhibition capacity of conducting polymers. The structural behaviour of electrochemically synthesized polymers has to be verified with the chemically synthesized samples. In the present course of investigation FT-IR spectroscopy is used for the structural comparison of the chemically and electrochemically prepared polymers. To explain the mechanism of corrosion protection, surface morphological studies is performed using scanning electron microscopy.

## CHAPTER 2

### MATERIALS AND METHODS

In this section details of procedures adopted for the polymeric coating on CS surface, treatment of the coated sample with the aggressive solution, methods used to study the effectiveness of polymeric coating in preventing the corrosion and characterization of the polymer, coated on the CS surface, are described.

#### **Chemicals**

Amino compounds such as aniline, 2-aminobenzene sulphonic acid, 2-aminobenzoic acid, 3-aminobenzoic acid, o-nitroaniline, m-nitroaniline and 2-aminophenol were procured from Merck Millipore. HCl (Merck) was used as the medium of polymerization.

#### **Metal specimens**

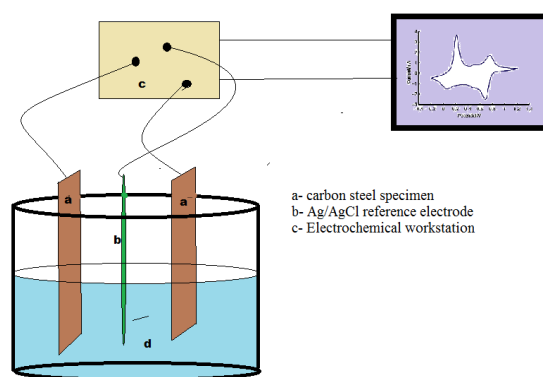
Carbon steel specimens were polished with various grades of SiC papers (120, 400, 600, 800, 1000, 1500 and 2000) cleaned with soap solution and degreased by acetone. The approximate composition of the steel specimen was determined by EDAX technique (C,0.55%; Mn,0.08%; P,0.04%; S,0.012%; Si,0.02% and rest Fe - Hitachi SU6600 model SEM).

#### **Polymeric coating on Fe surface**

#### **Electrochemical polymerization**

Cyclic voltammetric technique was used to coat the polymer on carbon steel surface (Figure 3.1). 0.2M amino compound was prepared in 1.0M HCl solution. 50 ml of this solution was taken in a beaker. Two Fe electrodes having  $2.25\text{cm}^2$  (exposed) areas were immersed in the solution. Ag/AgCl electrode is

also inserted into the cell to act as reference electrode. Using this three electrode assembly, cyclic voltammetry was performed using a potential range of -2.0 to +0.2 V. To get effective coating of polymeric amines on CS surface, the CV was repeated for 10 cycles. After the experiment, the Fe surface was taken from the cell, washed with distilled water and dried for 15 minutes in hot air oven kept at 90°C.



**Figure 3.1** Electrode assembly in cyclic voltammetric technique

### Chemical polymerization

A 1.0M solution of the aniline/substituted aniline (100ml) was prepared in 1.0M HCl. The temperature of the solution was kept between 0-5°C. To this solution 100ml 1.0M solution of ammonium persulphate in 1.0M HCl was slowly added, and kept the solution for precipitation. The precipitated product was filtered, washed with acetone and dried at 100°C for 1hour.

### Electrochemical studies

Iviumcompactstat-e electrochemical workstation controlled by ivium soft software was used for the electrochemical studies<sup>54-56</sup>. Corrosion protection power

of the coated CS samples were screened at two different conditions i) the coated steel specimen was kept for 24 hours in air and then immersed in 1.0M HCl for attaining open circuit potential (OCP). ii) the coated portion of the metal specimen was directly immersed in 1.0M HCl (100ml) for 24hours. An uncoated sample was also treated with 1.0M HCl for the same period. The following electrochemical investigations were conducted using the samples.

### **Potentiodynamic polarization studies**

For Tafel polarization study, three electrode cell assembly was used. Saturated calomel electrode (SCE) acted as reference electrode. Platinum and metal specimen (both having exposed area 1cm<sup>2</sup>) acted as counter and working electrodes respectively. Potentiodynamic polarization studies were carried out in the potential range +250 to -250mV with a sweep rate of 1mV/s. The corrosion protection efficiencies of the coated polymers were calculated from the corrosion current densities using the following equation

$$\eta_{\text{pol}} \% = \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100 \quad (3)$$

where  $I_{\text{corr}}$  and  $I'_{\text{corr}}$  are the current densities of uncoated and coated CS respectively<sup>57,58</sup>.

### **Electrochemical impedance spectroscopy (EIS) studies**

1KHz to 100mHz frequency range with an amplitude of 10mV was employed for electrochemical impedance studies. From the charge transfer resistance values, corrosion protection efficiencies were evaluated using the equation



$$\eta_{\text{EIS}} \% = \frac{R_{\text{ct}} - R'_{\text{ct}}}{R_{\text{ct}}} \times 100 \quad (4)$$

where  $R_{\text{ct}}$  and  $R'_{\text{ct}}$  are the charge transfer resistances of coated and uncoated CS respectively<sup>59</sup>.

### **IR spectral studies**

The polymeric film coated on the carbon steel specimens was carefully scratched with a stainless steel blade and performed FT-IR spectral studies using KBr pellet method in the range  $4000\text{-}400\text{cm}^{-1}$  using Shimadzu IR Affinity-1 model FTIR spectrophotometer. To ensure the deposition of the polymers, the surface film IR spectrum was compared with the IR spectrum of the chemically synthesized polyanilines.

### **Surface morphological studies**

To determine the modifications occurred to steel surface coated with polyamino compounds, on keeping in HCl for 24h, scanning electron microscopic studies were performed (JEOL JSM-6390LV/JED-2300). Micrographs of bare steel surface, uncoated specimen treated with 1.0M HCl for 24h etc were also captured and compared.

### CHAPTER 3

## CORROSION INHIBITION STUDIES OF POLYAMINO COMPOUNDS AS PROTECTIVE COATINGS ON CARBON STEEL IN 1.0M HCl

Various amino compounds were coated as polymeric material on carbon steel specimens using cyclic voltammetry. The cyclic voltammogram of Polyaniline [PANI], Poly(2-aminobenzoic acid) [P2ABA], Poly(3-aminobenzoic acid) [P3ABA], Poly(2-aminobenzene sulphonic acid) [P2ABSA], Poly(2-nitroaniline) [P2NA], Poly(3-nitroaniline) [P3NA] and oligomeric compound of 2-aminophenol [P2AP] are given in the Figure 3.2. Simple skeletal structures of polymeric samples coated on CS surface are given in the Table 3.1.

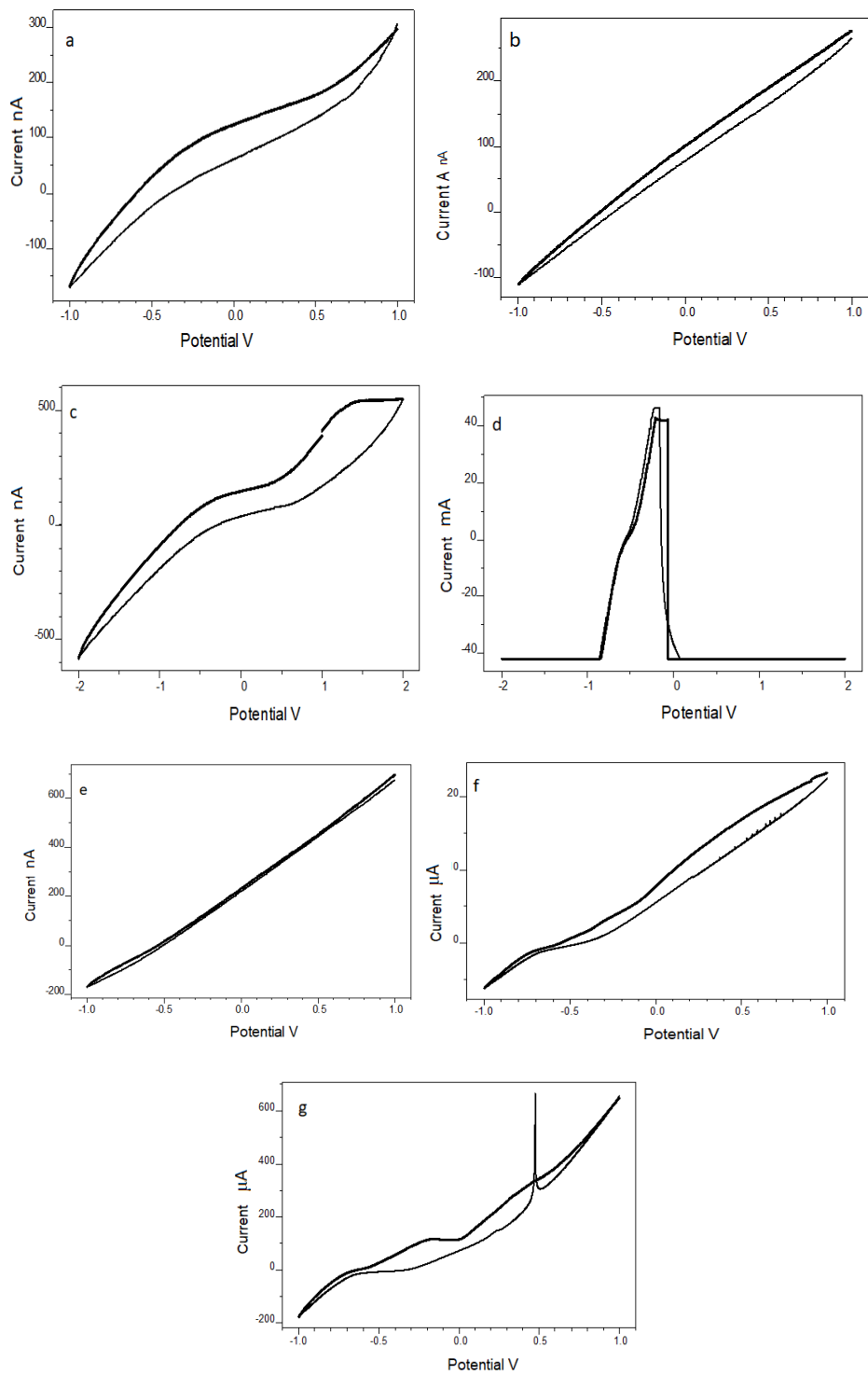
The polymeric structures were characterized using cyclic voltammetry. Some of the polymeric thin films didn't display well defined anodic or cathodic peaks in voltammogram. This can be attributed to the poor conducting nature of the polymers. Substituted polyanilines are generally less conducting than PANI<sup>60,61</sup>. The electronic propagation through the polymeric chains is considerably affected by the electron withdrawing or electron releasing nature of the substituents. Apart from this, steric hindrance in the substituted polyanilines will lead to the change in spatial arrangement of benzene rings which in turn causes decrease in the conductivity of the polymer.

The redox peaks appeared in CV plots of certain polymers gives clear indication of the formation of polymeric materials on carbon steel. The CV diagram of PANI displayed only a single oxidation peak at about -0.2 mV. This may be due to the oxidation of aniline into the emeraldine form (Figure 3.3). The

absence of the second oxidation peak can be explained due to the incomplete oxidation of PANI into its higher oxidation form perinigraniline. Since no well defined reduction peak was in the CV plot, it can be assumed that there is no appreciable reduction took place for PANI in HCl medium. Thus conversion of leucoemeraldine into to emeraldine is mainly taking place during the potential scanning process.

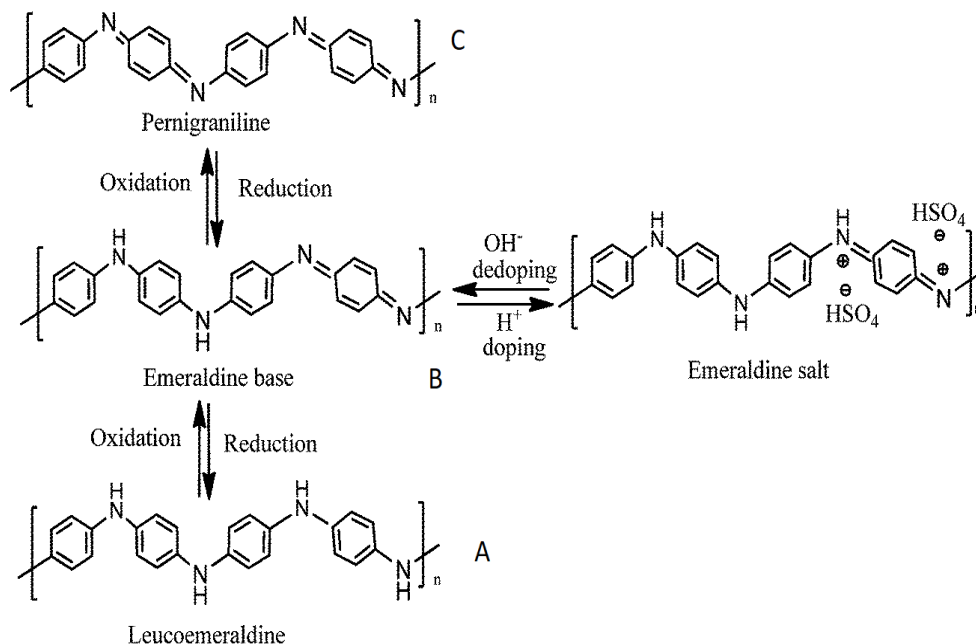
**Table 3.1** Name, abbreviation and skeletal structures of electrochemically synthesized polyamino compounds

Polymer	Abbreviation	Structure
Polyaniline	PANI	
Poly(2-aminobenzoic acid)	P2ABA	
Poly(3-aminobenzoic acid)	P3ABA	
Poly(2-amino benzenesulphonic acid)	P2ABSA	
Poly(2-nitroaniline)	P2NA	
Poly(3-nitroaniline)	P3NA	
Poly(2-aminophenol)	P2AP	



**Figure 3.2** Cyclic voltammograms of a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP

Poly(2-aminobenzoic acid), P2ABA did not give well defined redox peaks in CV diagram. This may be due to the weak conductivity of the polymer. Poly(3-aminobenzoic acid) displayed two distinct oxidation peaks at -0.3V and 1.3V in cyclic voltammogram. The first oxidation peak is due to formation of leucoemeraldine type non-conducting form of polymer (A in Figure 3.3). This on further oxidation converts into a more conducting form B. The second oxidation peak appeared at ~ 1.3 V is a strong evidence for the formation of the structure B. A reduction peak at 0.75 V was also visible in the CV diagram of P3ABA. This may be due to the reversion of emeraldine form B into leucoemeraldine form.



**Figure 3.3** Schematic diagram for the conversion of various forms of PANI

Poly(2-aminobenzenesulphonic acid), exhibited an unusual CV diagram in which only one oxidation peak was visible at approximately -0.32V. The current density at this potential was very appreciable which indicates the easiness of

oxidation process. No complete loop was seen in the CV diagram. The broad oxidation peak appeared in the CV plot can be believed to be due to the formation of both leucoemeraldine and emeraldine forms of poly(2-aminobenzenesulphonic acid). In the case of polynitroanilines also, well defined redox peaks were not appeared in CV diagrams, may be due to the very weak conductive power of these polymers.

### **Electrochemical studies**

Electrochemical corrosion investigations were done on the polymeric coated carbon steel specimen at two different conditions, i) the coated steel specimen was kept for 24h in air and immersed in 1.0M HCl for attaining open circuit potential (OCP) and the electrochemical tests were conducted. ii) the coated portion of the metal specimen was immersed in 1.0M HCl (100ml) for 24h, and electrochemical studies such as impedance spectroscopy and polarization analyses were performed.

### **Electrochemical impedance spectroscopy (EIS) studies**

Figures 3.4 & 3.5 and Tables 3.2 & 3.3 showed the Nyquist plots and impedance parameters of the coated metal specimen at two different conditions such as (i) kept 24h in air and immersed in 1.0M HCl and (ii) kept 24h in HCl medium respectively. All Nyquist plots were almost perfect semicircles<sup>62</sup>. The simple equivalent circuits, Randles circuit and Warburg impedance circuit will mimic the electrochemical system and can be used for the evaluation of impedance parameters<sup>63,64</sup>. For uncoated metal specimens the Randles equivalent circuit was used, while for coated metal the circuit used was Warburg impedance

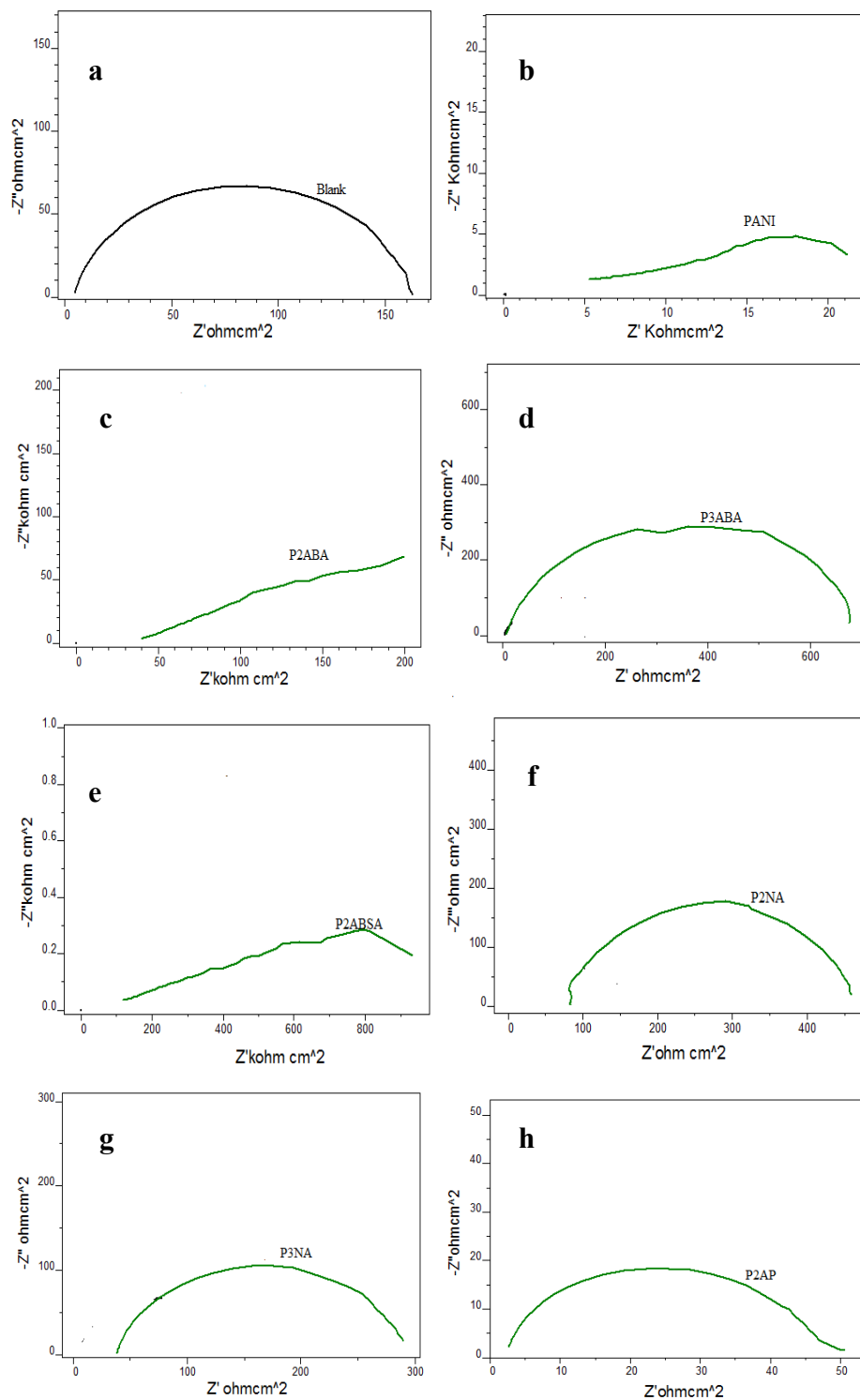
circuit. The Randles circuit consists of an electrolytic resistance ( $R_s$ ) in series with the parallel combination of charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) which can be represented as shown<sup>65</sup> in the Figure 3.7. The Warburg impedance circuit composed of  $R_s$ ,  $R_{ct}$ , and  $C_{dl}$  along with coating resistance ( $R_{coat}$ ) and Warburg resistance ( $W$ ) is given in the Figure 3.8.

**Table 3.2** Electrochemical impedance parameters of CS specimens coated with polyamino compounds kept for 24h in air and treated with 1.0M HCl

Sample	$C_{dl}$ ( $\mu Fcm^{-2}$ )	$R_{ct}$ ( $\Omega cm^2$ )	$R_{coat}$ ( $\Omega cm^2$ )	$W$ ( $\Omega cm^2$ )	$\eta_{EIS}$ (%)
Uncoated	114.7	149	-	-	-
PANI	$2.19 \times 10^{-3}$	1548	$1.88 \times 10^4$	$4.10 \times 10^4$	90.37
P2ABA	$1.91 \times 10^{-4}$	60100	$3.44 \times 10^5$	$2.10 \times 10^5$	99.74
P3ABA	$2.24 \times 10^{-4}$	628	$6.25 \times 10^2$	$1.79 \times 10^2$	76.27
P2ABSA	$1.09 \times 10^{-4}$	61400	$1.01 \times 10^6$	$1.09 \times 10^6$	99.75
P2NA	$2.45 \times 10^{-4}$	294	$3.77 \times 10^1$	$2.87 \times 10^1$	49.32
P3NA	$2.55 \times 10^{-4}$	200	$2.20 \times 10^1$	$1.67 \times 10^1$	25.5
P2AP	$3.66 \times 10^{-4}$	112	$1.03 \times 10^1$	5.44	-33.03

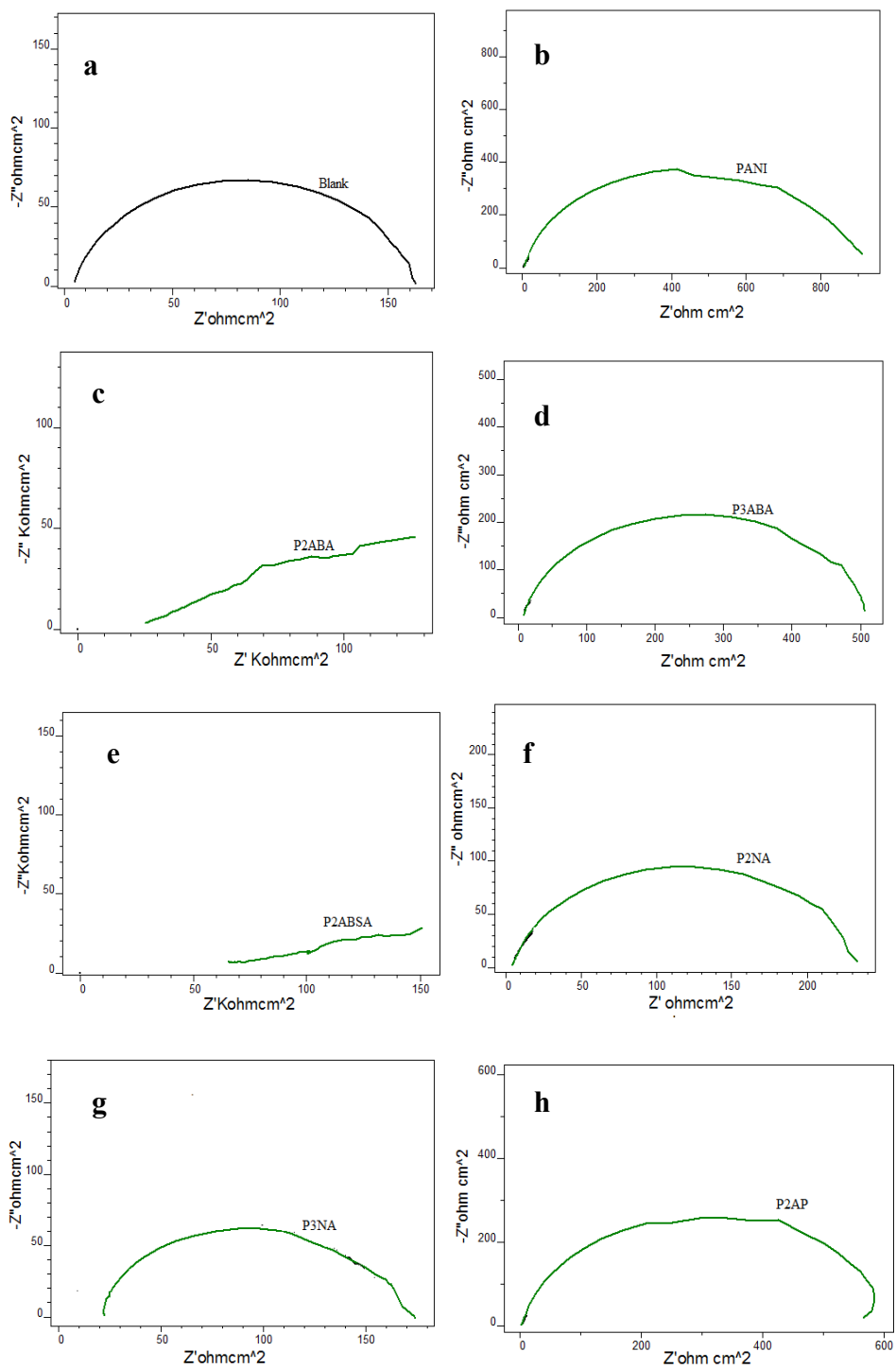
**Table 3.3** Electrochemical impedance parameters of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h

Sample	$C_{dl}$ ( $\mu Fcm^{-2}$ )	$R_{ct}$ ( $\Omega cm^2$ )	$R_{coat}$ ( $\Omega cm^2$ )	$W$ ( $\Omega cm^2$ )	$\eta_{EIS}$ (%)
Uncoated	114.7	149	-	-	-
PANI	$9.46 \times 10^{-5}$	760	$1.88 \times 10^4$	$4.84 \times 10^2$	80.39
P2ABA	$2.57 \times 10^{-5}$	17100	$3.44 \times 10^5$	$1.22 \times 10^5$	99.12
P3ABA	$8.31 \times 10^{-4}$	430	$6.25 \times 10^2$	$1.82 \times 10^1$	65.34
P2ABSA	$1.27 \times 10^{-5}$	56000	$1.42 \times 10^5$	$2.75 \times 10^5$	99.73
P2NA	$2.17 \times 10^{-4}$	194	$3.77 \times 10^1$	9.20	23.19
P3NA	$5.76 \times 10^{-4}$	106	$2.20 \times 10^1$	5.61	-40.56
P2AP	$1.83 \times 10^{-4}$	549	$3.31 \times 10^4$	9.19	72.85



**Figure 3.4** Nyquist plots of CS specimens coated with various polyamino compounds kept for 24h in air and treated in 1.0M HCl  
a) blank b) PANI c) P2ABA d) P3ABA e) P2ABSA f) P2NA g) P3NA h) P2AP





**Figure 3.5** Nyquist plots of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h a) blank b) PANI c) P2ABA d) P3ABA e) P2ABSA f) P2NA g) P3NA h) P2AP

From table 3.2 and 3.3 it is quite clear that all CS samples (except poly(2-aminophenol) coated) coated with various poly amino compounds showed appreciable corrosion protection efficiencies in 1.0M HCl. According to the previous studies it is established that conducting polymers act as a corrosion protecting material in two ways. First of all they can act as a physical barrier between the metal surface and surroundings to protect the corrosion, since the strongly adsorbed polymeric material will not allow the entering of the protons towards the metal surface. Thus the direct contact between the metal surface and the aggressive medium is very much reduced. Secondly the conducting polymers will make an electronic barrier on the surface.

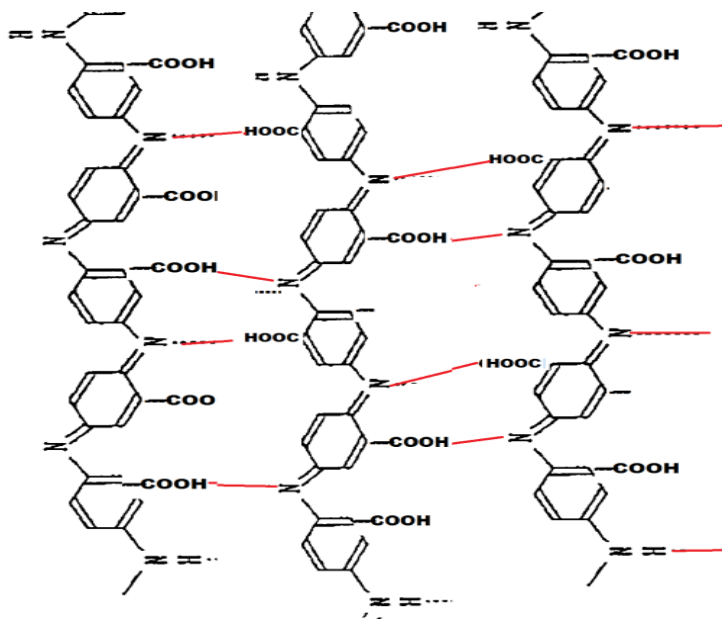
Conductive polymers are able to oxidize the metal surface and make passive oxides. This allows the shifting of the potential of the coated metal more towards cathodic side. Thus the metal will be protected. According to EIS studies, the protective efficiency of coated polymers on steel surface decreases in the order P2ABSA=P2ABA>PANI>P3ABA>P2NA>P3NA >P2AP in the case of condition 1(CS specimens coated with various polymers, kept for 24h in air and treated in 1.0M HCl). But the CS specimens coated with various polymers and treated directly with 1.0M HCl for 24h (condition 2) showed slight variation in the above order as P2ABSA= P2ABA>PANI>P2AP > P3ABA > P2NA> P3NA.

Among the polymers studied, P2ABSA and P2ABA displayed >99% of corrosion protection ability, for a period of 24h. PANI showed 90% and 80% of corrosion protection efficiency on CS specimens at condition 1 and 2 respectively. The protection ability of PANI has been established by the various researchers.

But, the ortho substituted polyanilines like poly(2-aminobenzene sulphonic acid) and poly(2-aminobenzoic acid) displayed higher protection efficiency than the conventional conducting polymer polyaniline.

Though the native conductivity of the conducting polymers may decrease with the deviation of the molecular segment from co-planarity, considerable molecular interaction between the polymeric chains may be possible in the ortho substituted polymer. Due to ortho substitution the basicity of N atom will be enhanced appreciably and hence greater interaction occurs between metal atom and the polymer. About cent percentage corrosion inhibition efficiency was shown by P2ABSA at both conditions. Similarly P2ABA also displayed very high corrosion inhibition on steel rebar surface. As per the mechanism, conducting polymers will inhibit the corrosion by two processes. Making a protective film on the metal surface and providing electronic barrier to prevent the oxidation. Since the native conductivity of polymer of ortho substituted amino carboxylic acid and sulphonic acid is low, compared to the unsubstituted polyaniline, it can be argued that P2ABSA and P2ABA make very strong protective layer on carbon steel surface. Strong intermolecular force of attraction of these molecules makes a uniform thin layer on steel surface. The P2ABA showed intermolecular H-bonding which is represented in the Figure 3.6 (Red line indicates H-bonds). Since the protecting efficacies of these polymers were high on CS surface at two different conditions; it can be assumed that these polymeric samples are highly stable to air and acid for a long period.

PANI also exhibited high corrosion inhibition value on CS surface for 24h (90% at condition 1 and 80% at condition 2). But compared to P2ABSA and P2ABA, it showed relatively less inhibitive power. Due to the conducting nature of PANI it makes an electronic barrier for oxidation of the metal in acidic medium. Thus it can be concluded that conductivity of a polymer is not the sole criterion to prevent the corrosion, but other factors like intermolecular attraction, uniform deposition of the polymeric film etc will also play a vital role in their corrosion inhibition capacity.



**Figure 3.6** Intermolecular hydrogen bond in P2ABA

P2NA and P3NA displayed 49% and 26% corrosion protection efficiency on CS surface at condition 1. Lower inhibition efficiency of these molecules than the previously discussed polymers is due to the presence of electron withdrawing nitro group on the benzene ring. Though these polymers provide poor electronic barrier for corrosion, they can make thin protective layer on the CS surface.

Intermolecular attraction between the polymeric chains due to the dipole interaction of the nitro groups makes the polymer to build a uniform thin protective layer on CS surface. The protection efficiency of P2NA and P3NA coatings were decreased to 23% and -40% respectively when the CS samples were exposed to the acid for 24h (condition 2). This implies that the stability of these coatings was poor in acidic medium. P3NA showed corrosion accelerating behavior at condition 2. This can be attributed to the complete decomposition of this polymer upon keeping in the aggressive medium for a long time.

Poly(3-aminobenzoic acid) displayed 76% of corrosion inhibition efficiency at condition 1. Though the protection efficacy is not very low, it is somewhat less than the inhibition efficiency of P2ABSA and P2ABA. This may be due to weak intermolecular force of attraction between the molecules. The meta carboxylic acid group present in P3ABA is not effective in making intermolecular forces. The electron density of aromatic ring present in the compound is not effective in making a strong adsorbed layer on the metal surface. This may be the reason why it displayed relatively less inhibition efficiency than the benzenoid aromatic polymers discussed earlier. At condition 2, P3ABA showed 65% of protection efficiency. This may be due to the less stable nature of this polymer in acidic medium

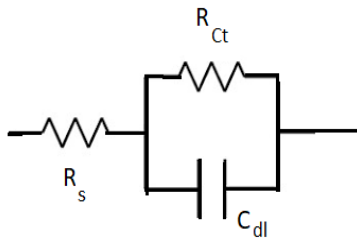
Among the corrosion behaviour of the polymers studied, poly(2-aminophenol) showed very low protection efficacy on CS in HCl medium at condition 1. Negative value of protection efficiency indicates the corrosion accelerating behavior of the material. Even though the hydroxyl group present in

the ortho substituted polymer is highly active, this material displayed poor protection capacity. 2-aminophenol has a strong tendency to get oxidized in the presence of oxidants in acidic and neutral media. Hadi Beiginejad et. al., using cyclic voltammetric investigations, established that, in acidic medium, aminophenols undergo electrochemical oxidation and convert into quinone molecules followed by hydrolysis, which leads to form a dimer<sup>66</sup>. From this work it can assure that 2-aminophenol molecules do not make any protective layer on CS surface during electrochemical polymerization. Instead of polymeric layer, oligomers or simple oxidized molecules like quinones derived from 2-aminophenol may adhered on the surface, leading to poor corrosion inhibition efficiency. On contrary to this, significant increase in the protective power of this coating was noted at condition 2. On continuous exposure of this coated CS sample to 1.0M HCl, decomposition may start for the polymeric/oligomeric materials to produce lower molecular weight species. This molecular species will start to dissolve in HCl medium and finally diffuse back to the metal surface and adsorb. Thus the decomposed product will behave as normal organic inhibiting molecules. This may be the reason why P2AP coated sample displayed very high protection efficiency when exposed to HCl for 24h.

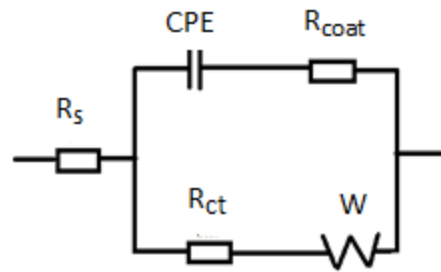
On examining the double layer capacitance of various coated polymers on CS surface, it can be understand that in general, as the  $C_{dl}$  value decreases, the protection efficiency of the polymeric coating increases. This behaviour can be correlated with the thickness of coating of polymer on CS surface. The analysis of

EIS data is done with the help of electrical equivalent circuits which represent the electrochemical processes occurring at the sample/electrolyte interface.

The Nyquist plots of all polymeric samples displayed well defined semi-circles. Randles circuit for uncoated metal specimen (Figure 3.7) and Warburg impedance circuit (Figure 3.8) were the fit equivalent circuit for the protection behaviour of coated material on CS.



**Figure 3.7** Equivalent circuit suitable for the uncoated metal specimens (Randles circuit)

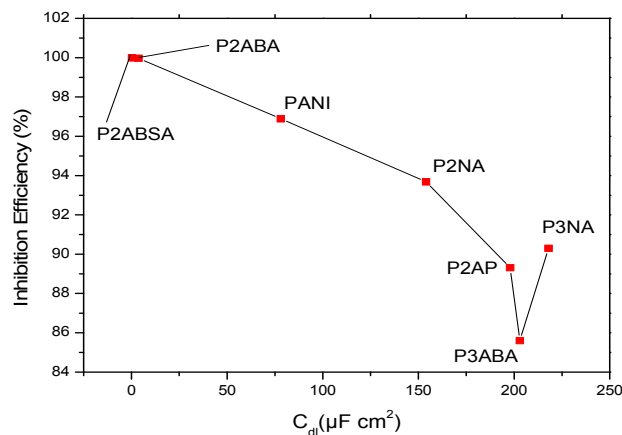


**Figure 3.8** Equivalent circuit suitable for the coated metal specimens (Warburg impedance circuit)

An intact coating mimics a dielectric material and can be treated as a capacitor. When the coating comes in contact with water molecules, they start to absorb water molecules on its surface. The electrolyte will enter into the small pores of the coating and will try to interact with the metal. The simple equivalent circuit described above can be used to interpret the electrochemical system at this stage. In this circuit  $C_{dl}$  and  $R_{ct}$  can be considered as coating capacitance and pore resistance respectively.

The coating capacitance is given by  $C = \frac{\epsilon_0 \epsilon_r A}{d}$

where  $\epsilon_0$  is the permittivity of the free space,  $\epsilon_r$  is coating dielectric constant or relative permittivity,  $A$  is the coating surface area and  $d$ , its thickness. From this equation it is clear that coating (double layer capacitance) is inversely proportional to the thickness of coating. This also implies that as the thickness of coating increases, the efficiency to protect the corrosion of the polymeric coating increases. In the case of coated samples the coating resistance ( $R_{\text{coat}}$ ) and Warburg resistance ( $W$ ) also increases with increasing inhibition efficiency. The double layer capacitance as a function of corrosion protection efficiency of various polymeric coatings at condition 1 (except P2AP) is plotted in the Figure 3.9.



**Figure 3.9** Double layer capacitance Vs corrosion protection efficiency of polymeric coated CS specimens in 1.0M HCl at condition 1

### Potentiodynamic polarization studies

To get an insight into the protection behaviour of polymeric materials on steel surface, potentiodynamic polarization studies were conducted<sup>67,68</sup>. This study was really helpful to evaluate the anodic/cathodic/mixed type corrosion inhibiting characteristics of the coated polymers. Polymerization studies were performed in



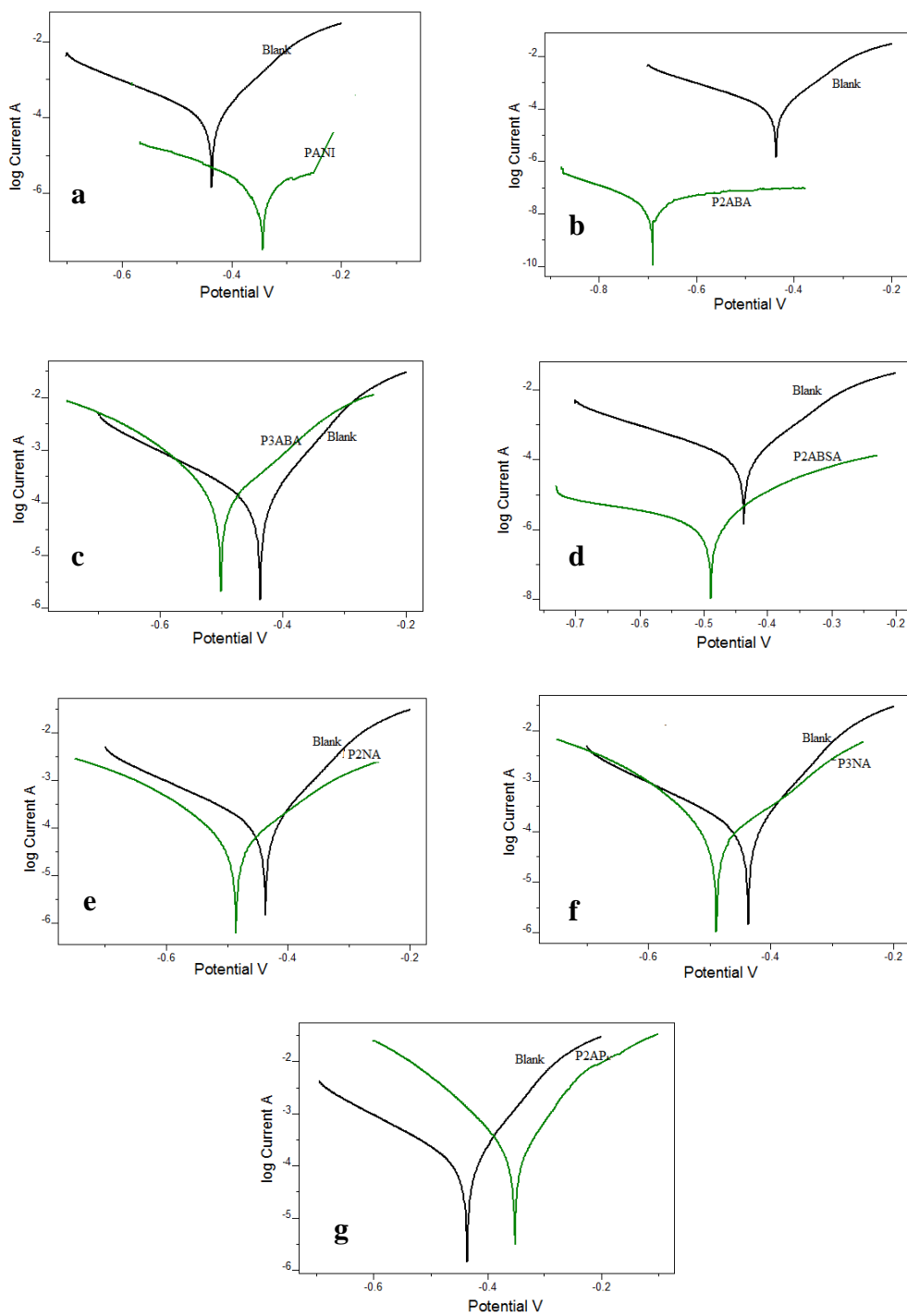
two different conditions. Coated specimens were kept for 24h in air and then immersed in 1.0M HCl (condition 1). In another manner, the metal specimen was directly immersed in 1.0M HCl (100ml) for 24h (condition 2). Then the polarization studies were carried out in the same medium. Polarization data along with protection efficiency of the various polyamino compounds at conditions 1 and 2 are given in the Tables 3.4 and 3.5 respectively. Polarization curves (Tafel curves) of various coated CS specimens are given in the Figures 3.10 and 3.11.

**Table 3.4** Tafel data of CS specimens coated with polyamino compounds kept for 24h in air and treated with 1.0M HCl

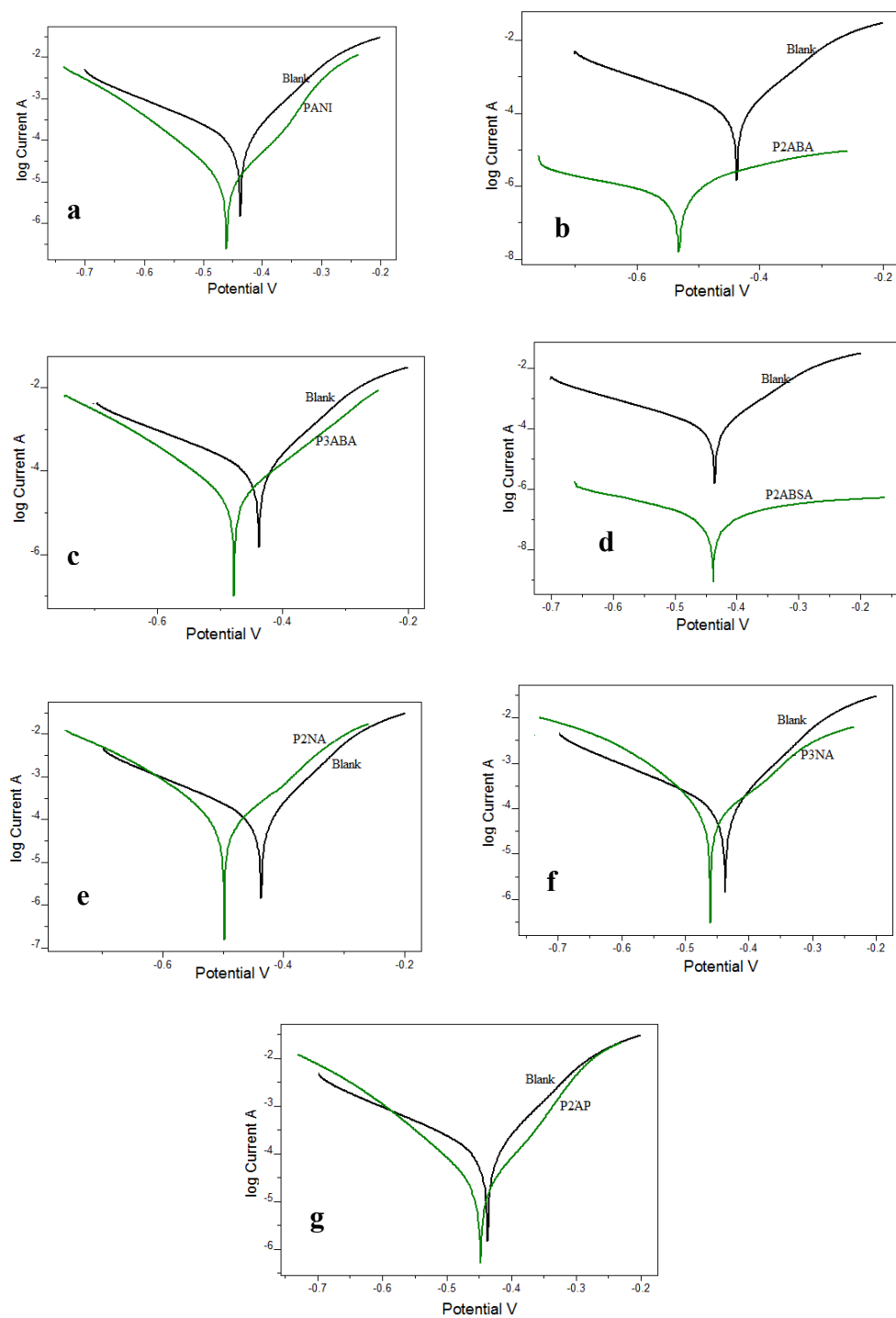
Sample	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$b_a$ (mV/dec)	$b_c$ (mV/dec')	$-E_{corr}$ (mV)	$\eta_{pol}$ %
Uncoated	111.4	83	173	439	-
PANI	0.671	37	187	343	99.39
P2ABA	0.0367	685	155	720	99.96
P3ABA	44.00	275	256	508	60.50
P2ABSA	1.956	142	328	519	98.24
P2NA	60.8	117	152	468	45.42
P3NA	94.75	104	145	453	14.94
P2AP	417.8	132	113	377	-27.5

**Table 3.5** Tafel data of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h

Sample	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$b_a$ (mV/dec)	$b_c$ (mV/dec)	$-E_{corr}$ (mV)	$\eta_{pol}$ %
Uncoated	111.4	83	173	439	-
PANI	8.70	53	101	433	92.18
P2ABA	0.74	260	300	578	99.33
P3ABA	24.48	86	109	468	78.02
P2ABSA	0.129	424	210	460	99.88
P2NA	81.6	79	125	471	26.75
P3NA	114.7	86	140	423	-2.96
P2AP	20.67	55	101	428	81.44



**Figure 3.10** Tafel plots of CS specimens coated with polyamino compounds kept for 24h in air and treated in 1.0M HCl a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP



**Figure 3.11** Tafel plots of CS specimens coated with polyamino compounds directly immersed in 1.0M HCl for 24h a) PANI b) P2ABA c) P3ABA d) P2ABSA e) P2NA f) P3NA g) P2AP

It is evident from the table that majority of polymers under study exhibited significant corrosion protective power on carbon steel surface. Among the seven samples coated on CS surface, PANI, P2ABA and P2ABSA exhibited more than 90% protection efficiency in both conditions. P3ABA displayed moderate efficiency of 60% and 78% in condition 1 and 2 respectively. The results obtained from EIS studies were comparable to that of polarization studies. The protective powers of the above mentioned polymers vary between 90-100%. The slight deviations observed between EIS and polarization studies may be explained by the change in redox behaviour of the coated polymeric materials upon sweeping of voltage in Tafel studies. It is well known that conducting polymers create electronic and physical barrier to fight against corrosion on the metallic surface. The electronic characteristics of these polymeric materials largely depend on the redox behaviour of the molecules. In polarization analysis there is an ample opportunity for a chemical species to modify its structural features due to the alteration of potential<sup>69,70</sup>.

For instance, according to EIS and polarization studies, P2ABSA and P2ABA displayed 99% corrosion protection efficacy on CS surface. On analyzing the above values, it is evident that there is considerable structural modification occurred in P2ABSA coating, during the potential scanning which will adversely affect the capacity of the polymer to make a very strong electronic barrier for preventing corrosion. But corrosion protection efficiency of PANI showed enhancement in Tafel studies than impedance studies. Sweeping of potential of PANI coated specimen may alter the redox behaviour of this coated material

which in turn cause improvement of the electronic barrier on steel surface. Among all the polymeric material, least corrosion inhibition nature was shown by P2AP coated CS specimen, which was kept 24h in air and then immersed in HCl medium. As explained in EIS studies, this is due to the inability of the amino compound to make a polymeric coating on the surface of CS in HCl medium. It is quite surprising that P2AP showed enhanced protection efficacy, when it was coated on CS sample and immediately exposed to aggressive HCl solution for 24h. P2AP (oligomer) is quite unstable and showed negative efficiency according to the condition 1. This behaviour may be due to the decomposition of the oligomer in HCl medium followed by the adsorption of the derived simple molecules on the metal surface.

Samples	Type of Inhibition
Uncoated	-
PANI	Mixed
P2ABA	Anodic
P3ABA	Mixed
P2ABSA	Mixed
P2NA	Mixed
P3NA	Mixed
P2AP	Mixed

**Table 3.6** Type of corrosion inhibition by polyamino compounds on CS specimen in 1.0M HCl in condition 1

One of the important polarization data is the values of slopes of Tafel lines. It is very useful to examine the anodic or cathodic or mixed corrosion protection behaviour of the adhered material on the metallic surface<sup>73</sup>. From Tables 3.6, it can be seen that the anodic and cathodic slopes of Tafel lines of coated CS samples showed significant shifts from that of blank specimens. A

prominent shift observed in the anodic slope of P2ABA with respect to the blank clearly indicates that this polymeric coating will purely inhibit the anodic process of corrosion (condition 1). All other coatings behaved more or less mixed protection behaviour on CS surface. i.e, they will uniformly decrease the rate of anodic as well as cathodic process of corrosion.

### **IR spectral studies**

In order to evaluate the structural characteristics of the coated polymeric materials on steel surface, the IR spectrum of the scratched film was compared with the IR spectrum of the chemically synthesized polymers. For chemical synthesis, ammonium persulphate in 1.0M HCl was used as the oxidant and the polymerization was conducted at 0-5<sup>0</sup>C. The time of addition of the oxidant was about 30 minutes. The precipitated polymeric materials were filtered, washed with water and dried.

Very good agreement was observed between the vibrational frequencies of coated polymer and chemically synthesized polymer. Even though, on close examination of the IR spectra of chemically and electrochemically synthesized polymers it was clear that the coated samples displayed frequency shift at certain specific area. This is a clear indication of the attachment of the polymeric substance on the metal surface through co-ordinate type bond. The similarities of the IR spectra of polymers synthesized by both methods indicated the structural agreement between the samples. The IR spectra of scratched polymeric film of all samples displayed a very strong absorption in the lower energy region which establishes the presence of strong interaction of the



**Table 3.7** Characteristic IR absorption frequencies of chemically and electrochemically synthesized polyamino compounds

Polymer	Chemically Synthesized (cm <sup>-1</sup> )	Electrochemically coated (cm <sup>-1</sup> )	Assignment
PANI	3012	3414	OH stretching/ N-H stretching
	1560	1564	C=C stretching of benzenoid ring
	1488	1488	C=C stretching of quinonoid ring
	1296	1290	C-C bending
	1130	1109	C-H bending (oop)/ring breathing
	820	-	C-H bending (out of plane)
P2ABA	3207	3433	N-H stretching
	1692	1637	C=O stretching
	1566	1548	C=C stretching of benzenoid ring
	1508	1458	C=C stretching of quinonoid ring
	1248	1382	C-C bending/N-H bending
	1048	1024	C-H bending
P3ABA	3228	3431	N-H stretching
	1691	1643	C=O stretching
	1574	1530	C=C stretching of benzenoid ring
	1508	1458	C=C stretching of quinonoid ring
	1304	1273	C-C bending/N-H bending
	1047	1024	C-O stretching
	827	-	C-H bending (oop)/ring breathing
P2ABSA	3348	3381	N-H stretching
	2905	2927	O-H stretching
	1641	1626	O-H bending
	1325	1262	C-C bending
	1163	1147	S-O stretching
	1113	1082	S-O stretching
	1059	1027	S-O asymmetric stretching
	897	-	C-H bending (oop)/ring breathing
P2NA	3377	3429	N-H stretching
	2906	2922	C-H stretching
	1631	1629	C=N stretching
	1508	1552	NO <sub>2</sub> asymmetric stretch
	1452	1463	N-H bending
	1340	1361	NO <sub>2</sub> symmetric stretch
	1056	1020	C-H bending
	890	846	C-H bending (oop)/ring breathing
	-	468	M-N bond stretching
P3NA	3348	3334	N-H stretching
	-	3146	C-H stretching
	1631	1616	C=N stretching
	1525	-	NO <sub>2</sub> asymmetric stretch
	1058	1020	C-H bending
	896	849	C-H bending (oop)/ring breathing
	-	473	M-N bond stretching
P2AP	3263	3350	N-H stretching
	3196	3203	C-H stretching
	1576	1472	Benzene skeletal
	1609	1622	C=N /C=C skeletal stretching
	1188	-	C-H in plane
	853	-	ring breathing



polymeric films with the surface metal atoms. The formation of M-N and M-O bonds is mainly responsible for the strong absorption in the region 600-450  $\text{cm}^{-1}$ . Compared to the FT-IR spectra of the chemically synthesized polymers, electrochemically prepared samples generally exhibited much broader peaks in the region 3000-3500  $\text{cm}^{-1}$ . This is due to the stretching vibrations of O-H groups mainly from the adsorbed water molecules on the coated polymeric film. The characteristic vibrational frequencies of functional groups were clearly visible in the IR spectrum of polymeric films.

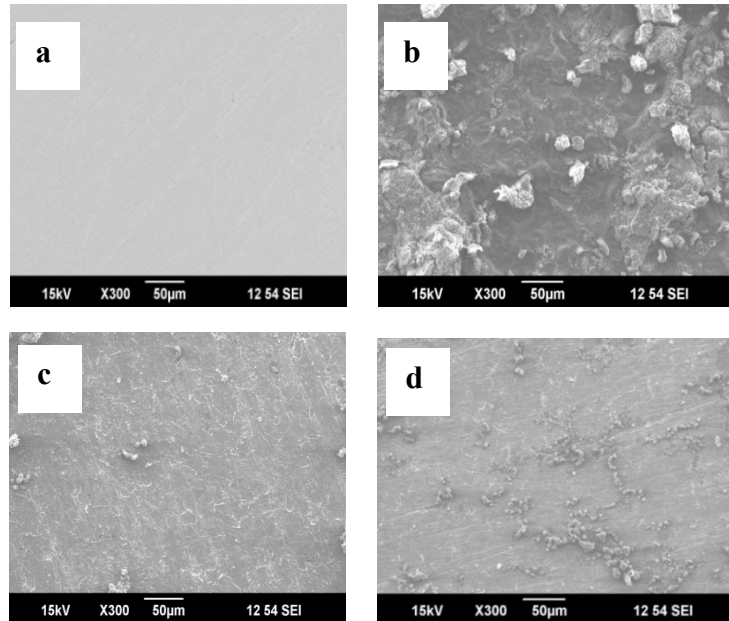
Table 3.7 compares the vibrational frequencies of polymers prepared by chemical and electrochemical methods. Figure 3.12 shows the overlay FT-IR spectra of polymers synthesized by chemical and electrochemical method.

### **Surface morphological studies**

To examine the morphology of the surface of the uncoated and coated steel specimens, scanning electron microscopic studies were conducted<sup>71,72</sup>. Figure 3.13 represent the micrographs of a) bare steel surface, b) steel specimen treated with 1.0M HCl for 24h c) P2ABSA coated steel specimen which was kept for 24h in air and immersed in 1.0M HCl d) P2ABSA coated steel specimen immersed in 1.0M HCl (100ml) for 24h.

The surface morphology of bare and blank specimens was entirely different. The surface of the blank specimen was irregular and rough due to the reaction between surface iron atoms and HCl. In the micrograph of the steel specimen coated with P2ABSA, the surface appeared to be smoother than blank

specimen (sample 1), indicating that a layer of polymer was strongly bound on the steel surface.



**Figure 3.13** SEM images of **a)** bare metal **b)** uncoated steel specimen immersed in 1.0M HCl for 24h **c)** P2ABSA coated steel specimen kept for 24h in air and immersed in 1.0M HCl **d)** P2ABSA coated steel specimen directly immersed in 1.0M HCl (100ml) for 24h

## SUMMARY

Seven amino compounds such as aniline, 2-aminobenzoic acid, 3-aminobenzoic acid, 2-aminobenzene sulphonic acid, 2-nitroaniline, 3-nitroaniline and 2-aminophenol were electrochemically polymerized in HCl medium using cyclic voltammetry. During the electrochemical process, the synthesized polymers were coated on the surface of the working electrode. Carbon steel specimen was used as the working electrode in cyclic voltammetry. The coated polymers were tested for their corrosion protection capacity in 1.0M HCl solution at two different conditions. In one condition, coated samples were dried, exposed to air for 24h and immersed in the aggressive medium and performed Tafel and EIS studies. Secondly the coated specimens were immediately immersed in 1.0M HCl for 24h and conducted Tafel and EIS studies.

Electrochemical analysis data both conditions established that the polymers PANI, P2ABA and P2ABSA possess very good corrosion protection efficiency (90-100%). The corrosion inhibition capacity of nitroaniline polymers was comparatively lower than that of the above mentioned polymers. This may be due to the decomposition of the layer formed on the CS surface in acidic medium. Comparatively less anticorrosive property was shown by P3ABA on CS surface. In condition 1, P2AP showed corrosion antagonistic behaviour, while in condition 2, the same polymer acted as very good corrosion inhibitor ( $\eta_{pol}\%$  81). This can be attributed to the decomposition of the oligomer of P2AP in to simple molecules at condition 2 which inturn adsorbed on the CS surface more effectively.

The structural characteristics of the electrochemically synthesized polymers were compared with the structural behaviour of the chemically synthesized polymers using FT-IR technique. From this study it was understood that the polymer molecules make appreciable chemical bonds with the surface metal atoms. To explain the mechanism of corrosion protection, surface morphological analysis was also done using scanning electron microscopy. Uniformly developed polymeric coating on the surface of CS was confirmed by the morphological study.