

Isomers of poly(aminothiophenol): Chemical synthesis and corrosion inhibition of mild steel in acidic medium

U. Anto Maria Jeraldin¹ and R. Jaya Santhi^{1*}

¹PG & Research Department of Chemistry, Auxilium College, Vellore, Tamil Nadu, India
amjeraldin@gmail.com, shanthijaya02@gmail.com

Abstract

The appositeness of conducting polymers to enrich the corrosion protection on metals in an acidic environment is building up greater significance as corrosion inhibitors. The isomers of poly(aminothiophenol) were synthesized by chemical oxidative polymerization method in aqueous HCl using ammonium persulfate as an oxidant. Electrochemical techniques such as potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss method were used to investigate the anticorrosion activities of the isomers of poly(aminothiophenol) on mild steel in 1M HCl solution. The results revealed that the inhibition effectiveness increased with increasing inhibitor concentration, with the greatest inhibition efficiency recorded for all three polymers at the optimum concentration of 500 ppm. Polarization investigations revealed that these poly(aminothiophenol) isomers function as mixed type corrosion inhibitors.

Keywords: Aminothiophenol, Conducting polymers, Corrosion, Mild steel, Electrochemical studies.

Introduction

Corrosion has a massive environmental impact, and its prevention has been extensively researched. The study of corrosion inhibition on mild steel is usually a topic of great theoretical and practical interest [1-3]. Mild steel (MS) is widely used in a variety of sectors for a wide range of applications, including chemical processing, petroleum production and refining, and marine applications. Mild steel in acidic medium is widely utilized in a variety of industrial processes, and mild steel corrosion is known to occur in acid solution. Corrosion in mild steel is a critical and costly issue in the industry, accounting for a significant amount of loss due to missed output, high maintenance, and inefficient operation. As a result, several corrosion inhibitors must be used to slow the degradation of mild steel. The anticorrosive compounds with heteroatoms in their structure can function as effective inhibitors for particular metals because they can build protective coatings on the surface [4-9].

The use of conducting polymers as anticorrosive compounds is gaining popularity due to their high inhibitory efficacy and inexpensive cost [10]. Poly(pyrrole), poly(aniline), poly(o-anisidine), and the derivatives of them have been broadly investigated due to ease of preparation, low energy for polymer formation, and their stability. It is expounded that the ring-substituted conducting polymers [11] can enhance the corrosion inhibition in aggressive environment. Previous research has disclosed that the corrosion prevention capabilities of poly(aniline) and its derivatives on metal corrosion in acidic media are due to their high molecular size, quaternary nitrogen atoms, and the availability of π electrons [12-14].

Aminothiophenols (ATP) are interesting electrochemical materials since both thiol and amine have different reactivities and thus provide more reactive sites. The successful use of this molecular assembly results in particular morphologies, which contribute to multi-purpose chemical strategies [15]. In theory, they could exhibit electrochemical activity

similar to anilines and/or thiols, with the relative position of the thiol and amino groups in the aromatic ring being a critical prerequisite for polymerization [16]. There is no article in the literature that we are aware of that deals with the corrosion resistance action of isomers of poly(aminothiophenol) on mild steel and other active metals.

In this paper, we report the synthesis of isomers of poly(aminothiophenol) (PATP) which is carried out by chemical oxidative polymerization method. An effort has been made to study the anticorrosion behavior of chemically synthesized poly aminothiophenols over MS in acidic medium by employing potentiodynamic polarization method (PDP), electrochemical impedance spectroscopy (EIS), and weight loss method and their results were compared.

Experimental

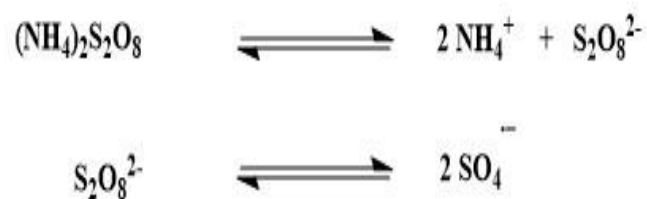
Synthesis of the polymers

The poly(o-aminothiophenol) (PoATP), poly(m-aminothiophenol) (PmATP), and poly(p-aminothiophenol) (PpATP) were synthesized by chemical oxidative polymerization method. Monomers (ortho-, meta-, and para-aminothiophenol), Ammonium persulfate (oxidant) were taken in the ratio of 1:2. The monomers were dissolved in 1M Hydrochloric acid. The aqueous solution of the oxidizing agent was slowly added into monomers solution. The solution was kept stirring for about 5 h at room temperature, after which the polymers were precipitated. The resultant polymers were washed with double distilled water till the filtrate was colorless followed by washing with methanol and acetone to discard the excess initiator, and oxidant. Finally, the resultant powders of PoATP, PmATP, and PpATP were then dried for 24 h [17]. The polymerization mechanisms of the synthesized polymers have given in Schemes 1, 2, and 3.

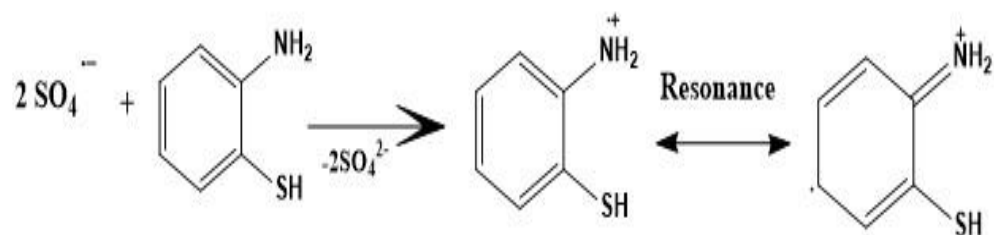
Specimen preparation

Mild steel specimens with the following compositions: 0.023 percent P; 0.04 percent Si; 0.017 percent Ni; 0.37 percent Mn; 0.078 percent C; 0.02 percent S; 0.002 percent Mo; Fe balance; were used. The specimen's dimensions are 3×3×0.1 cm and 1×1×0.1 cm, respectively, for weight loss and electrochemical tests. The specimens were embedded in epoxy resin, leaving a 1 cm² working area. Before each trial, the mild steel specimen's surfaces were abraded with various grades of silicon carbide emery papers (up to 1200 grit), followed by washing with acetone and rinsing with double-distilled water [18,19].

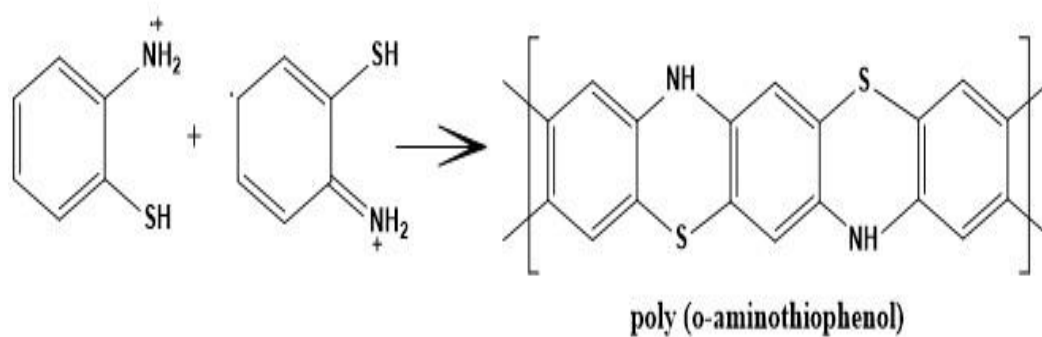
Step-I



Step-II

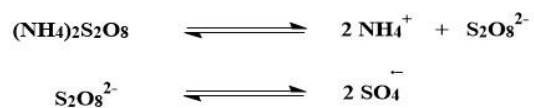


Step-III

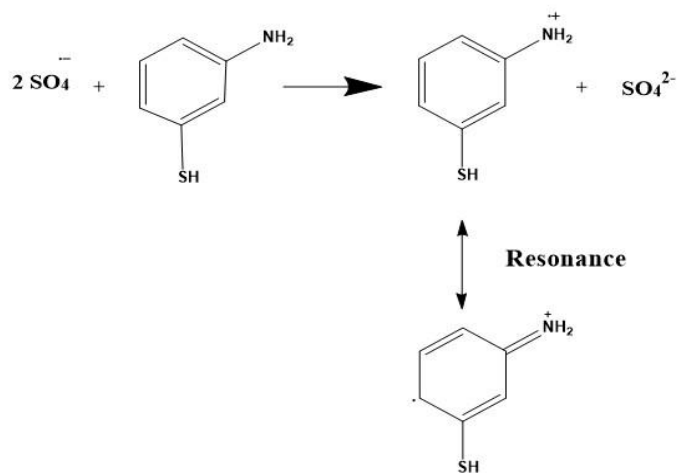


Scheme 1: Proposed mechanism of polymerization of o-aminothiophenol

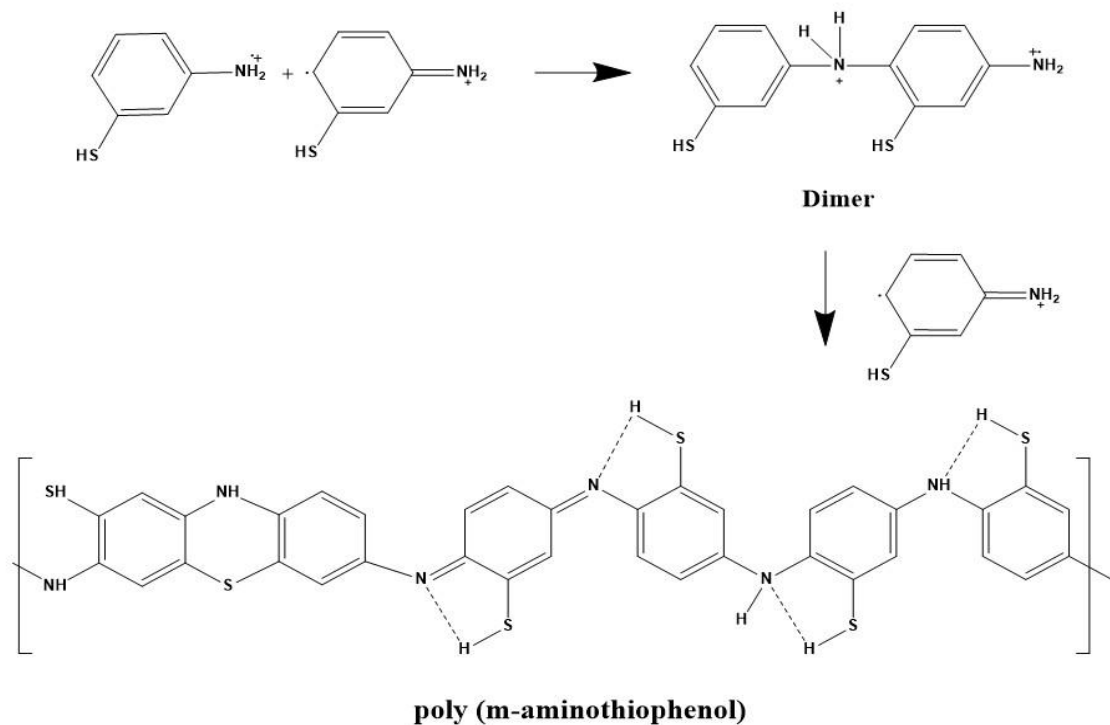
Step-I



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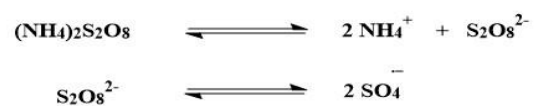


Step-III

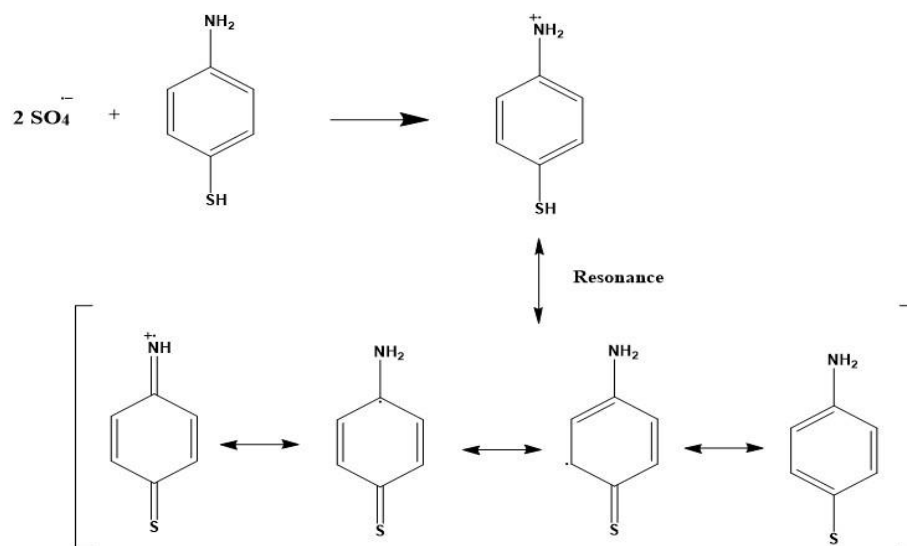


Scheme 2: Proposed mechanism of polymerization of m-aminothiophenol

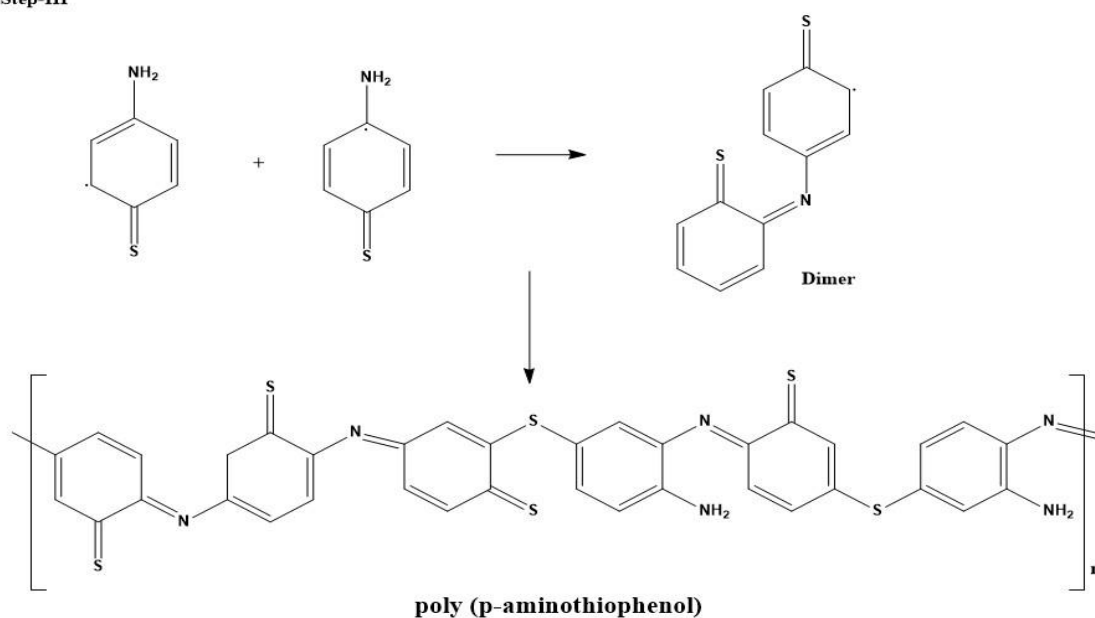
Step-I



Step-II



Step-III



Scheme 3: Proposed mechanism of polymerization of p-aminothiophenol

Electrochemical measurements

Electrochemical measurements, such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS), were performed in a three-electrode cell using the CHI 660E electrochemical impedance analyzer model. In the three-electrode framework Ag/AgCl was used, with 1M KCl as the reference terminal, a platinum electrode as the counter electrode, and a mild steel specimen as the working electrode. The mild steel was exposed to the solvent in an environment of around 1 cm². The electrode was allowed to corrode freely before each analysis of the potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS), and its Open Circuit Potential (OCP) was registered. The EIS experiments were carried out after a 30-minute immersion in the experimental solution, which meant that the system was in equilibrium. Following that, a steady-state of OCP corresponding to the working electrode's corrosion potential (E_{corr}) was obtained. At a scan rate of 10 mVs⁻¹, the potentiodynamic measurements were initiated from cathodic to anodic direction. After each sweep, a new inhibitor solution and mild steel specimens were used.

Weight loss method

Weight loss tests were performed in a beaker containing 100 ml of aerated 1M HCl solution at room temperature with varying concentrations of poly(o,m,p-aminothiophenol) for 3 hours of immersion and measured. At the conclusion of the experiments, the specimens were thoroughly washed in distilled water, cleaned, and measured. The weight loss of the mild steel samples was measured using an analytical balance with a precision of 0.0001. The experiments were carried out in triplicate, and the overall weight loss was reported.

Results and Discussion

Potentiodynamic polarization studies

The potentiodynamic polarization curves of mild steel in 1M HCl with varying concentrations of PoATP, PmATP, and PpATP are indicated in figures 1-3. Table 1 shows their electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), and inhibition efficiency (IE). The corrosion current density (I_{corr}) is determined by extrapolating the Tafel lines to the corrosion potential, and the inhibition efficiency (IE%) is calculated using the relationship:

$$\text{IE}\% = \left(\frac{I_{\text{corr}}^0 - I_{\text{corr}}}{I_{\text{corr}}^0} \right) \times 100$$

where, I_{corr}^0 and I_{corr} are the corrosion current densities in the absence and presence of inhibitor.

The potentiodynamic polarization curves in figures 1-3 clearly show that polymer addition prevents corrosion by regulating both the cathodic and anodic reactions. Polymer

molecules act as protonated species in acidic solutions, and these protonated species adsorb at the cathodic sites of mild steel, reducing hydrogen evolution [20]. Adsorption on anodic sites occurs through long π -electrons of aromatic rings such as benzenoid, quinonoid, and lone pair of electrons of nitrogen atoms, which reduces mild steel anodic dissolution [21,22]. As a result, the poly(aminothiophenol) isomers function as a mixed type inhibitor. The formation of an exceptional protective layer could be responsible for the E_{corr} trend in PATP [23]. The protecting layers of PATP isomers on mild metallic steel are especially due to the existence of a comparatively delocalized large π -electron structure in the aromatic ring, which coexists with a quaternary nitrogen atom, and their large molecular size, which endows them with many specific properties useful for a variety of applications [24-26].

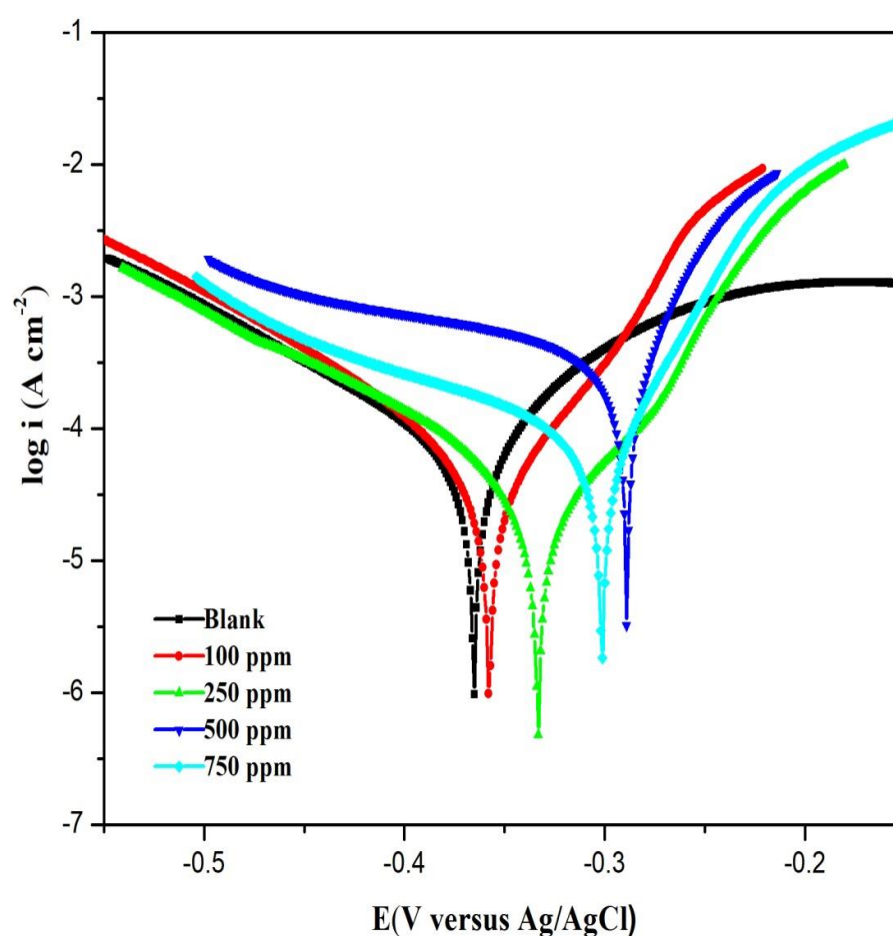


Figure 1. Tafel plots of PoATP at different concentrations

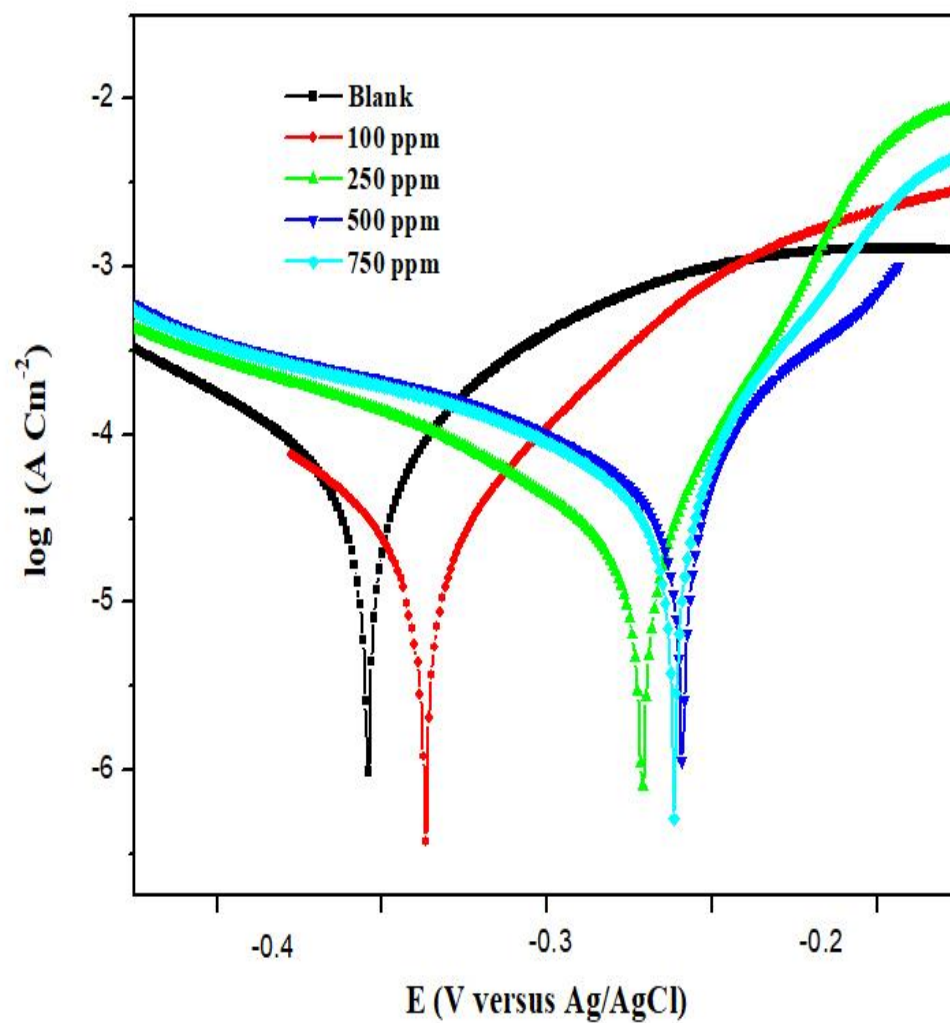


Figure 2. Tafel plots of PmATP at different concentrations

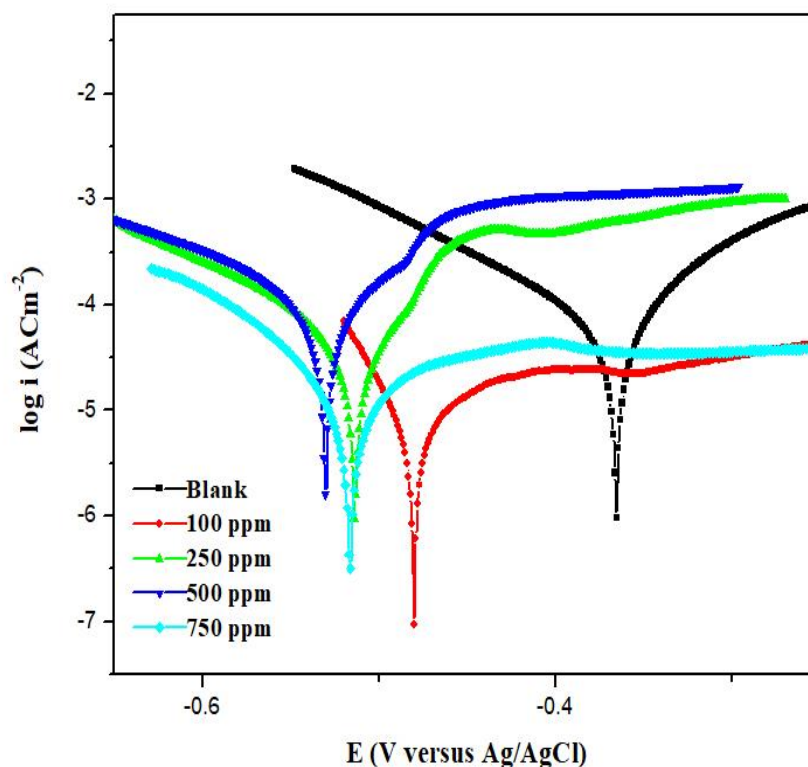


Figure 3. Tafel plots of PpATP at different concentrations

Table 1

Comparison of PDP parameters of isomers of poly(aminothiophenol)

Conc. (ppm)	PoATP			PmATP			PpATP		
	$-E_{corr}$ (mV)	I_{corr} ($\mu A/cm^2$)	% IE	$-E_{corr}$ (mV)	I_{corr} ($\mu A/cm^2$)	% IE	$-E_{corr}$ (mV)	I_{corr} ($\mu A/cm^2$)	% IE
Blank	364	125.1	-	364	125.1	-	364	125.1	-
100	358	40.9	67.30	344	61.4	50.91	480	61.7	50.67
250	333	26.7	78.65	265	41.0	67.22	513	49.5	60.43
500	289	14.8	88.16	250	26.7	78.65	530	22.1	82.33
750	301	22.7	81.85	254	37.3	70.18	516	35.6	71.54

According to the table values, the corrosion current density (I_{corr}) values decrease with increasing concentrations from 100 ppm to 500 ppm for all polymers, indicating that the polymers are adsorbed on the metal surface and hence inhibition occurs. The inhibition efficiency rises to 88.1%, 78.6% and 82.3% as PoATP, PmATP and PpATP concentrations rise from 100 to 500 ppm. Further increase in concentration leads to increase in the I_{corr} value with decrease in the inhibition efficiency, which shows that 500 ppm is the optimum concentration for all the three polymers.

Furthermore, the outstanding corrosion resistance provided by PoATP on mild steel can be attributed to the fact that the deposited polymer is firmly adherent and evenly covers the entire electrode surface. Moreover, isomers of poly(aminothiophenol) are ladder polymers with a longer molecular structure and a phenazine skeleton, ensuring better adsorption on the mild steel surface and reducing the effective area for the corrosion reaction by blocking the reaction sites [27].

Electrochemical impedance spectroscopy

The Nyquist impedance plots are analyzed by fitting the experimental results to a simple equal circuit model as given in figure 4. In the equivalent circuit model (Fig.4), R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE is a Constant Phase Element, that's placed in parallel to charge transfer resistance element.

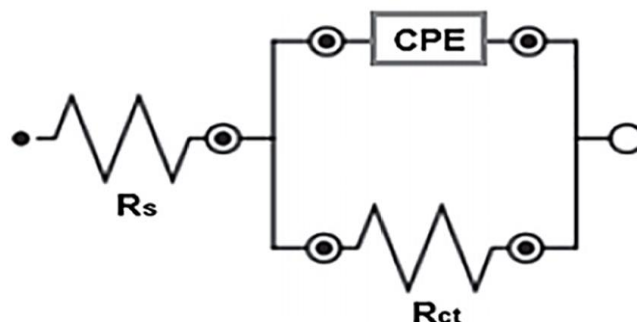


Figure 4. Equivalent circuit applied for fitting of the impedance spectra

Thus, in those conditions pure double layer capacitors (C_{dl}) are better defined by a transfer function with constant phase elements to give a more accurate fit. At high frequencies, the intersection of the semicircle and the real axis yields the solution resistance (R_s) value. The difference in impedance at lower and higher frequencies is used to calculate the charge transfer resistance (R_{ct}). The following equation is used to determine the % IE using R_{ct} values:

$$\text{IE \%} = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100$$

where, R_{ct} and R_{ct}^0 are charge transfer resistance in presence and absence of inhibitor obtained from the electrochemical impedance diagrams. The Nyquist plots of mild steel in 1M HCl within the presence of different concentrations of PoATP, PmATP, and PpATP are depicted in figures 5 to 7 and the corresponding electrochemical impedance parameters are given in Table 2.

The impedance spectra of PATP show (figures 5-7) a large capacitive loop at higher frequencies and a modest inductive loop at lower frequencies. The capacitive loop reveals that the charge transfer of the corrosion process and double layer behavior are particularly important in the management of mild steel corrosion [28]. The inductive loop, on the other hand, may be attributed to the relaxation process caused by PATP adsorption on the electrode surface [29].

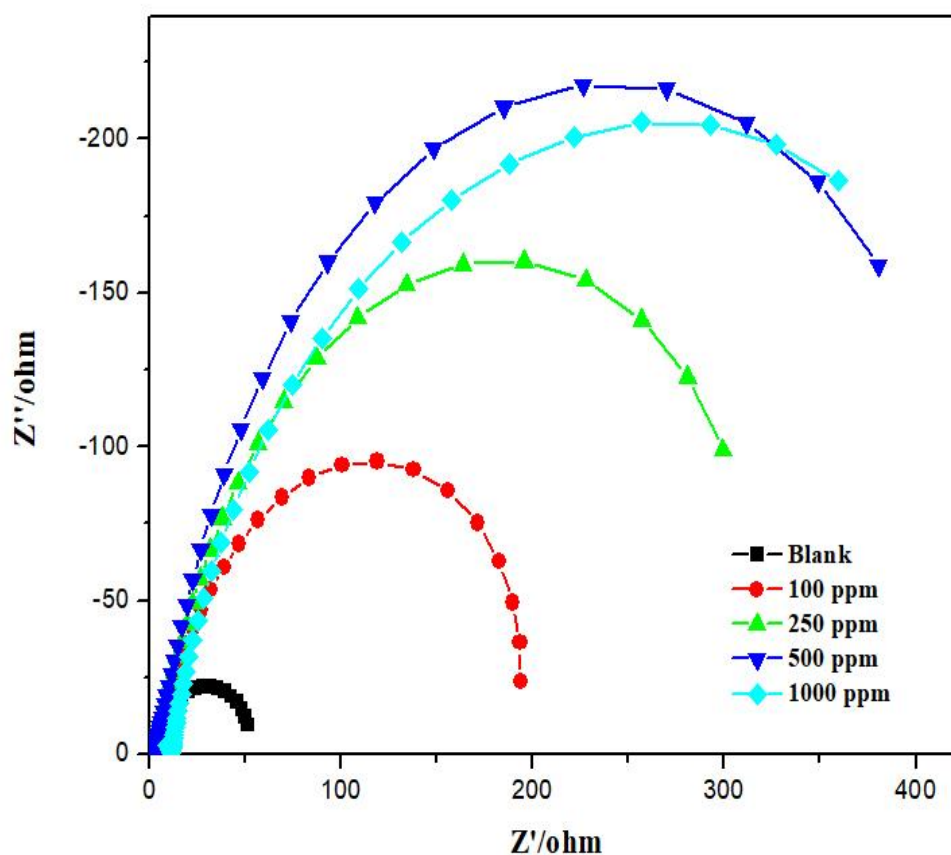


Figure 5. Nyquist plots of PoATP at different concentrations

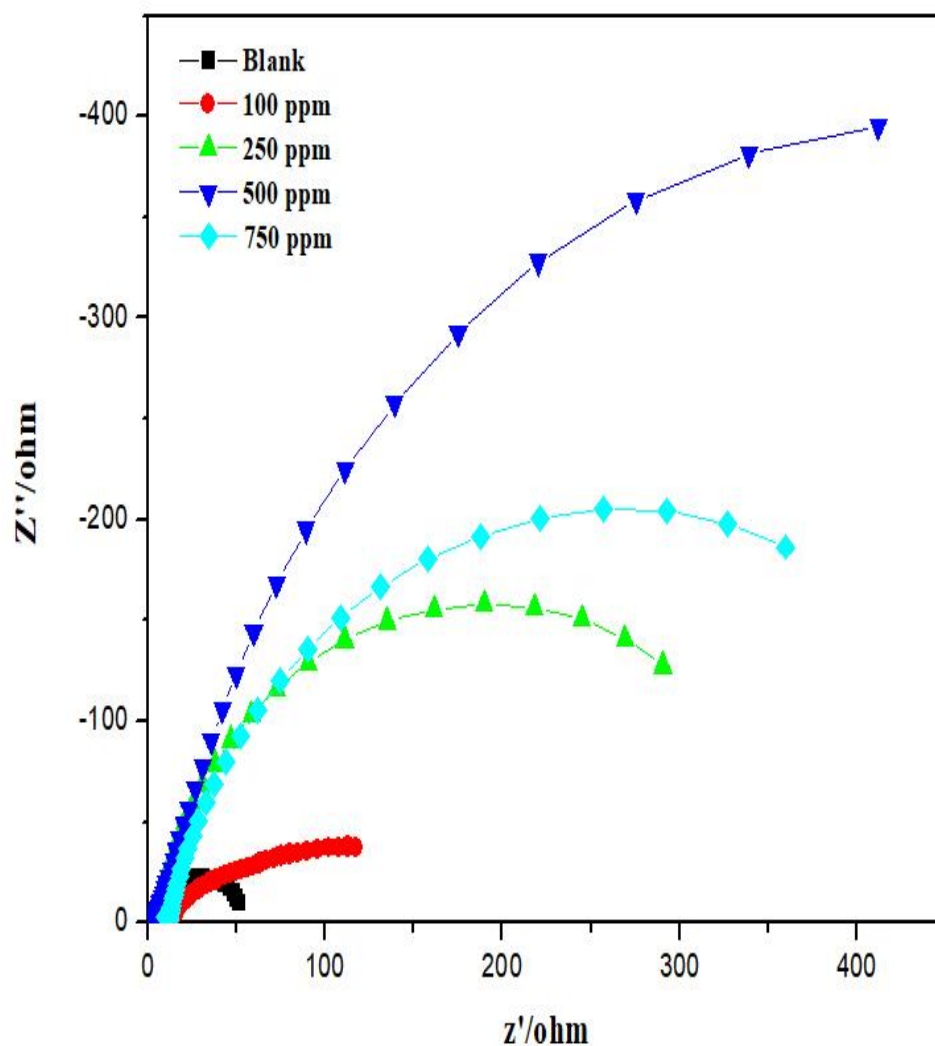


Figure 6. Nyquist plots of PmATP at different concentrations

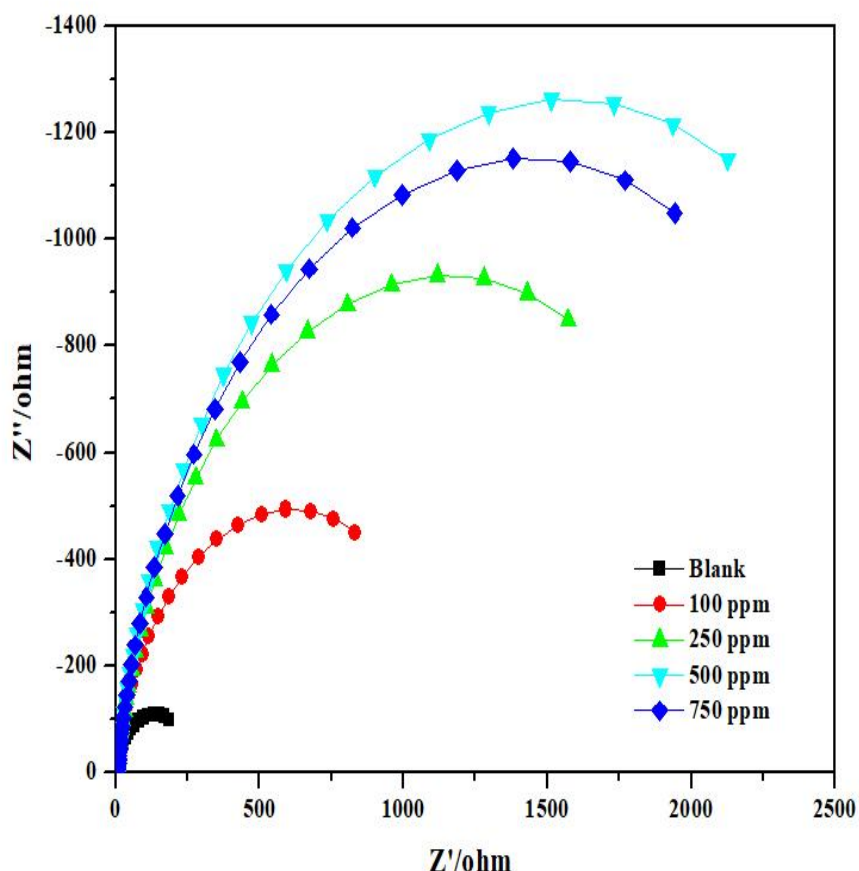


Figure 7. Nyquist plots of PpATP at different concentrations

The diameter of the capacitive loop is higher in the presence of PoATP, PmATP, and PpATP than in the absence of the same, which is a blank solution, implying that the impedance of mild steel rises with PATP concentration. The electrochemical parameters given in the Table 2 clearly show that the charge transfer resistance (R_{ct}) is increased from $36.43 \Omega\text{cm}^2$ to $598.1 \Omega\text{cm}^2$ for PoATP, from $36.43 \Omega\text{cm}^2$ to $147.4 \Omega\text{cm}^2$ for PmATP, and from $36.43 \Omega\text{cm}^2$ to $268.2 \Omega\text{cm}^2$ for PpATP at 500 ppm resulting in 93.9%, 75.2%, and 86.4% inhibition efficiency for the PoATP, PmATP and PpATP respectively. The development of an insulating protective film at the metal interface is attributable to the increase in R_{ct} values with increasing concentration [30].

The values of C_{dl} decreased with an increase of the inhibitor concentration up to 500 ppm. The drop in C_{dl} values with increasing polymer concentration is related to a drop in the local dielectric constant and an increase in the thickness of the electrical double layer. The C_{dl} values clearly demonstrate that the inhibitor functions through adsorption at the metal surface. The shift in C_{dl} values, on the other hand, is because of the gradual and slow

replacement of the water molecule through PATP adsorption on the metal surface and lowering the magnitude of metal dissolution [31].

Table 2
Comparison of EIS parameters of isomers of poly(aminothiophenol)

Conc. (ppm)	PoATP			PmATP			PpATP		
	C _{dl} (μF/cm ²)	R _{ct} (Ωcm ²)	IE (%)	C _{dl} (μF/cm ²)	R _{ct} (Ωcm ²)	IE (%)	C _{dl} (μF/cm ²)	R _{ct} (Ωcm ²)	IE (%)
Blank	102.2	36.43	-	102.2	36.43	-	102.2	36.43	-
100	94.8	107.3	66.0	76.8	61.71	40.9	95.6	61.27	40.5
250	75.3	194.8	81.3	43.8	78.56	53.6	70.1	109.3	66.6
500	19.2	598.1	93.9	16.3	147.4	75.2	49.0	268.2	86.4
750	22.7	253.3	85.6	31.5	111.4	67.3	65.7	160.0	77.2

The results also show that an increase in charge transfer resistance is associated with a drop in double layer capacitance up to 500 ppm of PATP's concentration. The effect is reversed when the concentration rises over 500 ppm. The corrosion resistance decreases when the concentration of isomers of poly(aminothiophenol) is increased above 500 ppm, indicating that 500 ppm is the optimum concentration for all three polymers PoATP, PmATP, and PpATP.

Weight loss method

Weight loss method is a physical measurement which gives direct result to the corrosive environments. The weight loss results of mild steel in 1M HCl with various inhibitor concentrations of PoATP, PmATP, and PpATP, as well as the blank solution, are obtained. It is observed that PATP prevents the corrosion of mild steel in 1M HCl solution at the concentrations utilized in this investigation. The inhibition efficiency (IE%) was estimated using the equation below.

$$IE\% = \left(\frac{W_0 - W_i}{W_0} \right) \times 100$$

where, W_0 and W_i are the weight of the mild steel in the absence and in the presence of inhibitor. In the weight loss method the percentage of corrosion inhibition efficiency increases on mild steel in 1M HCl solution to 78%, 68.8%, and 69.5% for PoATP, PmATP, and PpATP, respectively.

The inhibition efficiency increased as the inhibitors PATP concentration increased until it reached the optimum concentration of 500 ppm, beyond which the inhibition efficiency decreased. Above 500 ppm, inefficiency may be caused by a weakening of metal-inhibitor interactions, resulting in the replacement of inhibitor by water or chlorine ions, leading in a drop in inhibition efficiency [32]. From this result, it's obvious that the corrosive sites of mild steel surface get adsorbed by PATP which is accountable for their's anticorrosion activity. The adsorbed films of PATP function as a physical barrier among mild steel and corrosion medium. The inhibition efficiencies determined by electrochemical impedance spectroscopy and potentiodynamic polarization methods are associated with the IE determined by the weight loss method for all polymers, and all of the aforementioned measurements confirm that the %IE increased with PATP concentration.

Conclusion

The poly(o,m,p-aminothiophenol) were synthesized successfully through chemical oxidative polymerization method and the mechanism of formation is given. The anticorrosion behavior of poly(o,m,p-aminothiophenol) study led to the finding that isomers of PATP successfully prevent mild steel corrosion in 1M HCl solution. Poly aminothiophenols were shown to be a mixed type of inhibitors in polarization investigations. The charge transfer resistance increased with increasing inhibitor concentration, according to the EIS plots of mild steel. The % IE obtained by PDP and EIS were considerably equivalent with the weight loss method, and corrosion inhibition efficiencies were reduced in the following sequence PoATP > PpATP > PmATP. The inhibition was due to the adsorption of the inhibitors over the surface of mild steel which resulting in blocking off the active sites. Furthermore, the π -electrons conjugation, polymer size and quaternary nitrogen atom, promote their strong adsorption over MS, resulting in excellent protection of mild steel in extremely corrosive medium. The results of this anticorrosion investigation clearly show that isomers of poly(aminothiophenol) might be considered as a good choice as a corrosive inhibitor for mild steel in an acidic environment in the future.

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