



Potentiodynamic deposition of poly (*o*-anisidine-co-metanilic acid) on mild steel and its application as corrosion inhibitor

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ABSTRACT

For the first time, poly (*o*-anisidine-co-metanilic acid) (PASM) was deposited on mild steel substrate by electrochemical polymerization of *o*-anisidine and metanilic acid monomers in aqueous solution of 0.1 M H₂SO₄. The electrochemical polymerization of *o*-anisidine takes place in the presence of metanilic acid monomer and uniform, strongly adherent coating was obtained on the substrate. The electroactivity of copolymer was studied by cyclic voltammetry and AC impedance techniques. There is an increasing anodic current due to oxidation of metanilic acid monomer at the surface of the electrode when the applied potential is cycled from −0.2 V to 0.8 V. These deposits were characterized by Fourier transform infrared (FTIR) spectroscopy, UV–vis and TG/DTA techniques. The effect of various concentrations of PASM copolymer solution in acid rain corrosive media has been studied through potentiodynamic polarization, AC impedance and *I*–*E* curve methods. The soluble form of polymeric solution provided better anti-corrosive behavior in artificial acid rain solution.

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1. Introduction

The electrodeposition of conducting polymers on a predefined electrode surface has been a very active research area in electrochemistry for the last two decades. The great deal of interest in the area is due to the large number of potential applications of the conducting polymers and the modified electrode surfaces [1,2]. Thermodynamically, the electrodeposition of conducting polymer on oxidizable metal is a difficult process as the metal dissolves before the electropolymerization potential of the monomer is reached. Therefore it is necessary to find electrochemical conditions which lead to a partial passivation of the metal and decrease its dissolution rate in order to achieve the deposition of a conducting polymer on iron (or other oxidizable metals). Self-doped polyaniline derivatives present an important class of conducting polymers since they bear ionogenic SO₃H group. These negatively charged groups act as an intra molecular dopant anions that are able to compensate positive charges at protonated nitrogen atoms of the polymer backbone, thus replacing auxiliary dopant anions. The inner anion doping determines many distinctive properties of self-doped polyaniline (PANI), which differs from those of the parent polyaniline. Both chemical synthesis and electrochemical synthesis have been involved in preparing self-doped PANI derivatives. Apart from chemical synthesis, electropolymerization presents a versa-

tile technique in preparing self-doped PANI. Soluble self-doped polymers were obtained by anodic oxidation of *o*-, *m*- and *p*-amino benzene sulfonic acid [3]. Therefore, the more versatile technique seems to be the electrochemical copolymerization of at least two aniline co-monomers, one of them bearing sulfonate group.

Electrodeposition of polypyrrole and polythiophene was achieved on Fe from nitrate and oxalic acid solutions [4–6] as well as from organic solutions [7–9]. Camalet et al. [10] reported that passivation of oxidizable metals prior to electropolymerization is necessary to obtain an adequate adhesion of synthesized polyaniline film. Ahmad and MacDiarmid [11] noticed that PANI in the emeraldine oxidation state has adequate oxidation capability to passivate stainless steel (SS). Wessling [12] also reported that mild steel (MS), stainless steel and copper could be passivated by PANI. Lu et al. [13] deposited PANI on mild steel. PANI films are also deposited on mild steel from aqueous oxalic acid [14]. Several ring-substituted anilines namely *o*-toluidine, *m*-toluidine, *o*-anisidine and *o*-chloro aniline were electrodeposited on passivated surfaces [15]. Sazou and Georolios [16] studied electropolymerization of aniline on an iron disc electrode in aqueous solution by using various inorganic and organic acids under potentiodynamic, potentiostatic and galvanostatic conditions. Recently, poly (*o*-methoxy aniline) was electropolymerized on SS electrode by cyclic voltammetry and observed corrosion inhibition similar to PANI [17]. Moreover, the copolymer films of poly (aniline-co-*o*-anisidine) were carried out on copper electrode by cyclic voltammetric technique and their corrosion performances were also characterized [18]. Zin et al. [19,20] and Baghi et al. [21] studied anti-corrosion performances of inor-

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ganic ions on galvanized steel by acid rain and also established corrosion performances of acid rain solution on zinc. Sathiyarayan et al. [22] have also found that the soluble poly (ethoxy aniline) for corrosion inhibition behavior of iron in 1 M HCl solutions.

Studies related to copolymerization of anisidine are limited and its compatibility with metanilic acid is expected to yield a product that is different from aniline. Moreover the known solubility of polyanisidine has motivated to couple this with metanilic acid for making a copolymer. In order to make a comparative analysis, this paper presents the electrochemical polymerization method and its resultant characteristics as well as application in corrosion inhibitive role on mild steel. Thus the goal of this study is (i) to obtain adhering conducting copolymer of poly (*o*-anisidine-co-metanilic acid) by using a common metal such as mild steel and (ii) to examine the protection of iron against corrosion by using the obtained conducting copolymer solution. The result of the study shows that for the first time, the copolymer was deposited on active metal (MS) and the ability of copolymer to provide corrosion protection to mild steel in artificial acid rain corrosive media.

2. Electrochemical preparation of polymer deposits

Analytical grade chemicals namely, *o*-anisidine, H₂SO₄, and metanilic acid were used. *o*-Anisidine was vacuum-distilled before use. Triple distilled water was used for the preparation of solutions. Copolymer of *o*-anisidine and metanilic acid was deposited on mild steel (grade 304). A mild steel foil was polished with emery, washed with detergent, acetone, rinsed with triple distilled water and air-dried. Geometrical area of the electrode used for copolymer deposition was 1 cm². Electropolymerization was carried out in a supporting electrolyte of 0.1 M H₂SO₄-containing dissolved *o*-anisidine and metanilic acid of 3:1 mole concentration ratio, keeping the total concentration of 0.1 M.

A glass cell fitted with ground glass joints suitable for introduction of the working electrode, platinum foil as counter electrode and SCE reference electrode was employed. The deposition of copolymer was carried out potentiodynamically (PD). In the

having provisions for the inlet of nitrogen gas. A platinum electrode, saturated with calomel electrode and mild steel cylindrical rod was used as counter, reference and working electrodes, respectively. The potential of the working electrode was measured with respect to saturated calomel electrode (SCE) through lugging capillary.

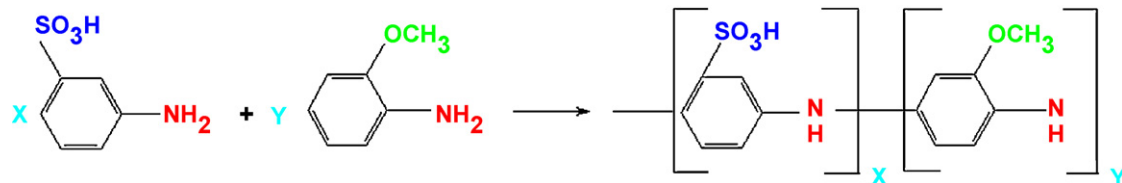
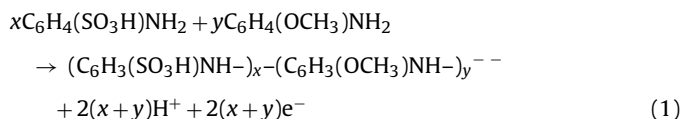
Electrolyte solutions were prepared with triple distilled water and deaeration of these electrolytes was carried out by bubbling purified nitrogen gas for 30 min. Experiments were carried out in an artificial rain solution containing 25–75 ppm of poly (*o*-anisidine-co-metanilic acid) polymeric compositions. Corrosion inhibition activity of the copolymeric solution on mild steel was monitored using potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) techniques.

2.2. Polarization studies

The potentiodynamic measurements provide a clear evidence of significant corrosion potentials provided to the exposed bare mild steel areas, galvanically coupled to the polymer coatings. The potentiodynamic polarization was examined by using BAS electrochemical analyzer (Model 100B). Three-electrode cell arrangements were used in which mild steel rod of 1 cm² area as a working electrode, a Pt foil as counter along with SCE reference electrode for recording potentiodynamic polarization. The copolymer was deposited on the mild steel and then scraped off to study its physical characterization by FTIR, UV-vis and TG/DTA techniques and discussed in detail.

3. Results and discussion

The electrochemical oxidation of *o*-anisidine and metanilic acid in aqueous acidic electrolyte produces copolymer of *o*-anisidine and metanilic acid according to the following reaction:



potentiodynamic method, the electrode was subjected to cycling between -0.2 V and 0.8 V, and the growth of the copolymer deposit to the required thickness was achieved by cycling 100–200 sweep rates at 50 mVs^{-1} . The deposition of copolymer was carried out using a computer-controlled BAS 100B electrochemical analyzer. The corrosion inhibition activity of the PASM copolymer was studied by using polarization technique, AC impedance spectroscopy (EG & G Instruments Model 6310) and I - E curves method.

2.1. Corrosion control measurements

Mild steel rod was used as test electrode for this study. The electrode was insulated with electrophoretic paint and then embedded with an epoxy insulator so as to expose the surface area of 1 cm^2 . The electrodes were mechanically abraded with a series of emery papers, followed by thorough rinsing in acetone, deionised water and drying in air. The corrosion cell, consisting of a three-electrode system, was made up of a double-walled glass cell of capacity 40 ml

As the reaction is an anodic oxidation process, the substrate metals generally employed are based on the noble metals [23,24]. However, it has been shown that electrodeposition of PANI can also be obtained on non-platinum metal substrates in spite of the fact that they undergo oxidation during the initial potential sweep [25]. The stainless steel substrate is already proven one for the deposition of a thin layer of PANI [26]. However, the use of mild steel is hitherto unknown and hence an attempt has been made to prepare the PASM by using MS anode. Fig. 1 shows cyclic voltammogram recorded during the synthesis of poly (*o*-anisidine-co-metanilic acid) on mild steel. The figure shows the formation and growth of the polymer film. The intensity of the two broad oxidation and reduction peaks of the film increases as the film grows.

3.1. Thermal analysis of PASM prepared by PD method

Fig. 2 shows the TG/DTA curves obtained for the copolymer PASM prepared by potentiodynamic method. The copolymer starts dehydrated from 74°C mainly due to the expulsion of water

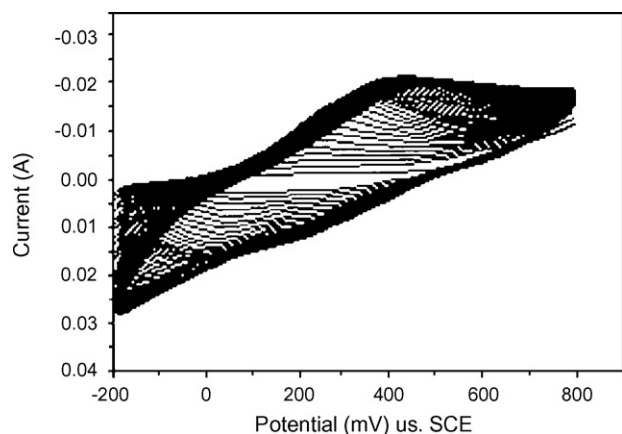


Fig. 1. Cyclic voltammogram record during the synthesis of poly (*o*-anisidine-co-metanic acid) on mild steel.

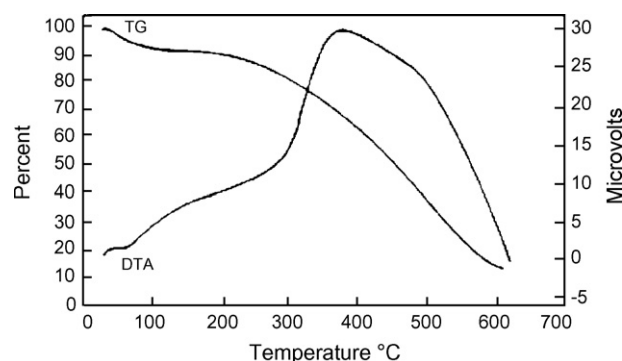


Fig. 2. TG/DTA curves of M prepared by potentiodynamic method.

molecules from the polymer matrix. The weight loss from 232 °C up to 608 °C reveals the degradation of the PASM copolymer backbone chain structures.

3.2. FTIR analysis

A close observation of the FTIR spectrum of copolymer is shown in Fig. 3. The peaks around 1600 cm^{-1} and 1500 cm^{-1} show wide variations in intensity and positions. The two bands are assignable to non-symmetric C_6 ring vibration bands [27].

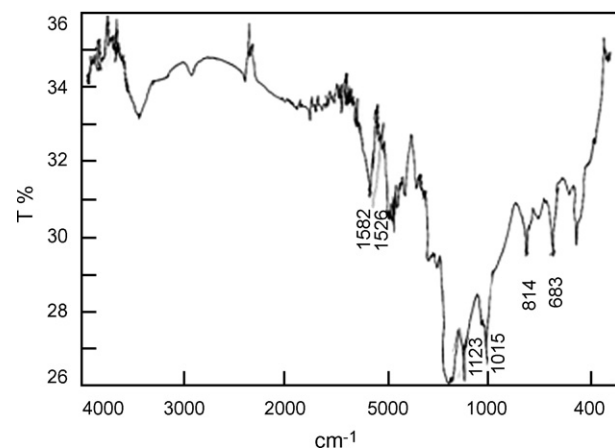


Fig. 3. FTIR spectrum of the PASM (in KBr-pressed pellet) obtained by potentiodynamic method.

The frequency vibration (1600 cm^{-1}) represents the quinoid ring and lower one (1500 cm^{-1}) represents the benzenoid ring. The presence of both bands implies that the copolymer possesses amine and imine units in the backbone. Both bands inform the presence of different extents of oxidation states in these copolymers. The peak at 1582 cm^{-1} and 1526 cm^{-1} agreed well with the literature [28] for the assignment of quinoid and benzenoid nitrogen structures. The incorporation of $-\text{OCH}_3$ group in the copolymer may have imparted increasing tendency to oxidize the amine units of the backbone. The peak at 1015 cm^{-1} assigned to the symmetrical stretching of the $\text{C}-\text{O}-\text{C}$ bonds due to the presence of *o*-methoxy groups in the copolymer structure [29]. The peak at 618 cm^{-1} indicates the presence of SO_3H group and 815- cm^{-1} peaks due to aromatic $\text{C}-\text{H}$ bending.

3.3. UV-vis spectroscopic analysis

The UV-vis spectrum of copolymer solution prepared by potentiodynamic method is shown in Fig. 4. The literature reveals that studies on the copolymerization of PASM are scarce. Only two spectral bands around 325 nm and 584 nm have been noticed for the copolymerization. Based on the assignment made for the polymerization of aniline derivative, the bands around 325 nm and 584 nm of PASM can be assigned for the polaronic and bipolaronic transitions [30]. The band around 325 nm is assigned to $\pi \rightarrow \pi^*$ (which corresponds to band gap) and the band above 500 nm is assigned to $\pi \rightarrow \pi^*$ exciton band or interband charge transfer associated with excitation of benzenoid to quinoid rings [31].

3.4. Electrochemical characterization of PASM copolymer

The PASM/MS electrode was characterized by obtaining cyclic voltammograms in 0.1-M H_2SO_4 blank solution at 2 mV s^{-1} , 5 mV s^{-1} and 10 mV s^{-1} scan rates shown in Fig. 5. Few interesting observations could be noticed on comparing the CVs of copolymer. For all the cases, redox transitions responsible for leucoemeraldine to emeraldine form could be seen. The mid point potential values for the redox process as well as current values, obtained from CVs are presented in Table 1.

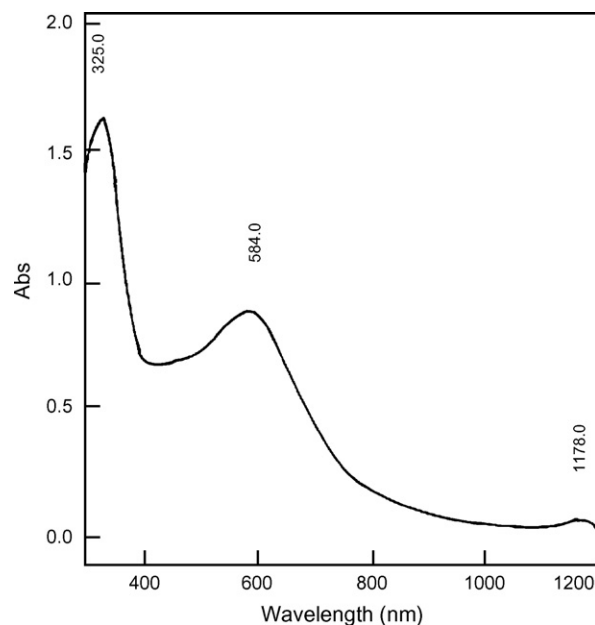


Fig. 4. UV-vis spectrum of PASM in NMP prepared by potentiodynamic method.

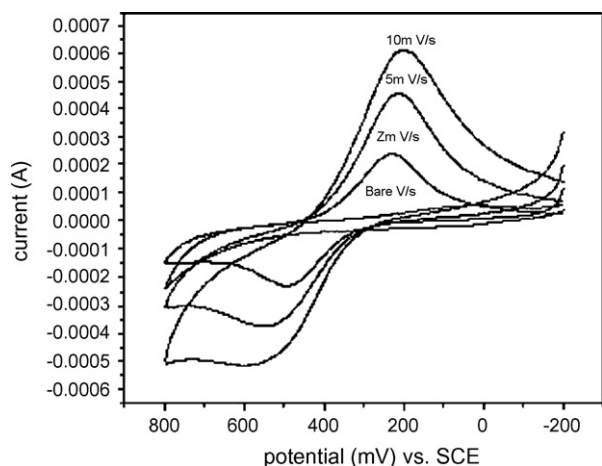


Fig. 5. Cyclic voltammogram of PASM/MS electrodes in 0.1-M H_2SO_4 at 2 mV s^{-1} , 5 mV s^{-1} and 10 mV s^{-1} scan rates.

The cyclic voltammogram of poly (aniline-co-anisidine) electrodeposition demonstrates similar redox processes of anisidine but differs in peak potential [18]. As can be seen in Fig. 1, the CV curves for the electrodeposition of poly (*o*-anisidine-co-metaniilic acid) grow with number of cycles which indicates the formation of conducting polymer. There is only one redox peak observed during the copolymerization of anisidine for all the scan rates. This shows that the oxidation potential of the monomer is dependent on size and type of the anion present. When the applied potential is cycled from -0.2 V to 0.8 V , there is an increasing anodic current which shows that the monomer is dissolving in the solution, oxidized at the surface of the electrode.

3.5. Impedance of PASM/MS electrodes

Fig. 6 shows the impedance spectra of PASM/MS electrodes recorded at 0.0 V , 0.2 V and 0.4 V potentials. Each spectrum is characterized by a high frequency intercept on the real axis, a semicircle and a linear Warburg part at middle frequency range and a vertical linear spike at low frequency. A steady increase in solution resistance R_s (Table 2) suggests that electrolyte present inside the pores is likely to have higher resistance due to the entry of anions into the polymer layer. It is interesting to observe that there is a decrease in capacitance element due to the thickness of the polymer layer.

The impedance spectra of PASM/MS electrode at 0.4 V potential at a sweep rate of 50 mV s^{-1} are shown in Fig. 6. This spectrum contains the 45° linear part. The high frequency interrupt on the real axis shows capacitive spike which appears immediately after the formation of semicircle. It is thus clear that the resistive part is smaller than that of the polymer resistance R_p in the case of potentiodynamically deposited electrode. The impedance spectra of PASM/MS electrodes at several applied potentials are found to have the similar shape. The impedance parameters are tabulated in Table 2 as a function of applied potential used for potentiodynamic

Table 1

CV parameters obtained for electrochemical copolymerization of PASM at different scan rates

Scan rate (mV s^{-1})	Peak potential (mV)			Peak current (mA)	
	Anodic E_p^a	Cathodic E_p^c	ΔE_p	Anodic I_p^a	Cathodic I_p^c
2	225	500	275	0.256	0.237
5	200	525	325	0.475	0.375
10	183	567	364	0.637	0.525

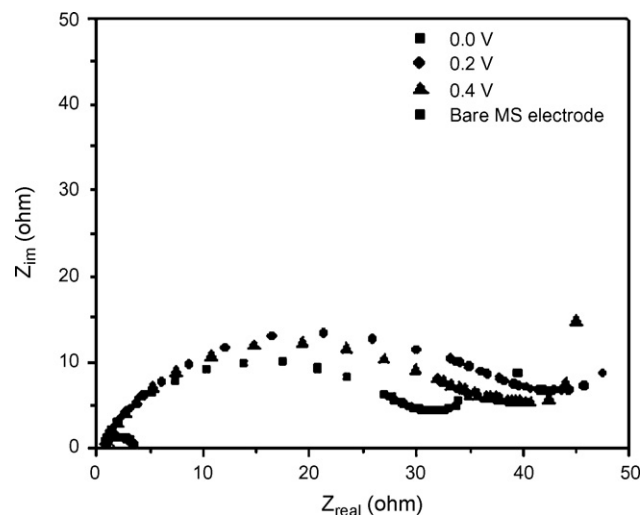


Fig. 6. Nyquist impedance spectra of PASM/MS electrodes in 0.1-M H_2SO_4 at 0.0 V , 0.2 V and 0.4 V vs. SCE.

deposition of PASM. There is an increase in R_s and R_p with increasing applied potential. The growth of the deposit takes place layer by layer, and each layer becomes electrochemically active before the next layer is deposited.

Hence, the PASM deposited by PD method is likely to be more efficiently activated since the polymerization is uninterrupted. It is not possible for the formation of branched chain of PASM during polymerization between consecutive sweeps.

3.6. Corrosion inhibition studies by polarization method

Corrosion rate (current) information could be obtained by using polarization technique, where the large cathodic and anodic polarizations provide the cathodic and anodic polarization curves for the respective corrosion process [32]. The observations of corrosion protection from the formation of passivating oxide layer by potentiodynamic polarization measurements provide a measure of the tendency of an alloy to undergo active/passive behavior [33]. The corrosion inhibition of PASM polymer solutions prepared from various concentration levels (25 ppm, 50 ppm and 75 ppm) was studied by using potentiodynamic polarization method. Fig. 7 shows the set of polarization curves recorded for the mild steel both in inhibitor free as well as inhibitor-added solution. The anodic and cathodic curves have been found to be well defined and the use of conducting solutions has been formed to shift the E_{corr} to a positive value. Table 3 lists the corrosion potential at various concentrations for mild steel sample exposed to the acid rain corrosive environment. From the table, it shows that E_{corr} shifts to a more positive value for 25 ppm, 50 ppm and 75 ppm polymeric solution approximately from 5 mV to 10 mV . Similarly, I_{corr} values have also been shifted to lower values for 25 ppm, 50 ppm and 75 ppm concentrations with respect to bare metals. R_{corr} values and inhibition efficiencies have been calculated and are given in Table 3.

Table 2

Impedance parameters for electrocopolymerization of PASM

Applied potential V	Polymer resistance R_p (Ω)	Capacitance C (μF)	Solution resistance R_s ($\text{m}\Omega$)
0.0	28.19	162	863
0.2	39.72	302	859
0.4	36.29	208	1008

Table 3
Corrosion parameters of mild steel in acid rain for PASM

Polymer concentration (ppm)	Corrosion potential E_{corr} (mV)	Corrosion current I_{corr} (μA)	Corrosion resistance R_{corr} (mpy)	Inhibition efficiency (%)
Bare	–570	234.12	108.11	–
25	–565	177.82	82.05	24
50	–564	144.54	66.69	38.26
75	–544	100.49	54.21	57.6

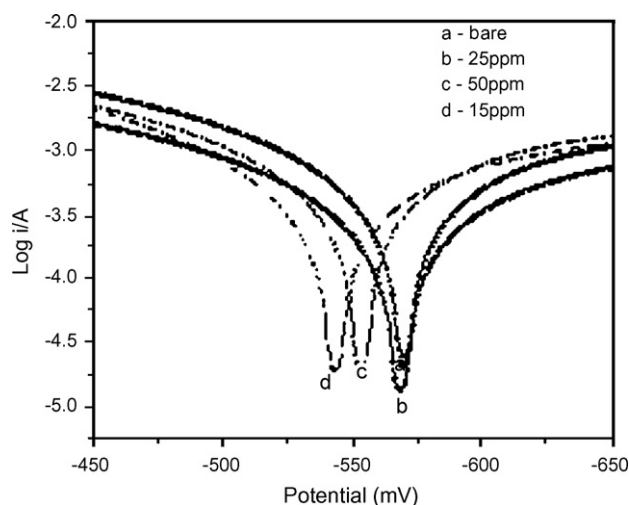


Fig. 7. Polarization curves for mild steel in acid rain solution inhibited by 25 ppm, 50 ppm and 75 ppm of PASM prepared by potentiodynamic method.

Measurements of corrosion potential E_{corr} , corrosion current I_{corr} (Fig. 7) relative to E_{SCE} provide an indication that the presence of PASM polymer solution on mild steel affects the corrosion process. Several interesting features are evident.

1. The mild steel-containing PASM polymer solution in acid rain at different concentration levels exhibited corrosion potentials more positive than the corresponding control sample.
2. The maximum shifts in corrosion potential were observed for the concentration of 75-ppm polymer solution.
3. The protection extends to bare mild steel is of significance and of commercial importance.
4. It is also evident that the levels of protection provided by PASM solution to mild steel depend on the nature of the form of the copolymer and the nature of corrosion environment.

3.7. Corrosion studies of PASM/MS acid rain through electrochemical impedance analysis

In Fig. 8 the Nyquist plots obtained for mild steel in acid rain PASM copolymeric solutions prepared by PD method are shown. The semicircle at high frequency can be assigned to charge transfer reaction. The charge transfer resistance R_{ct} is at the metal/electrolyte interface and C_{dl} is the double-layer capacitance

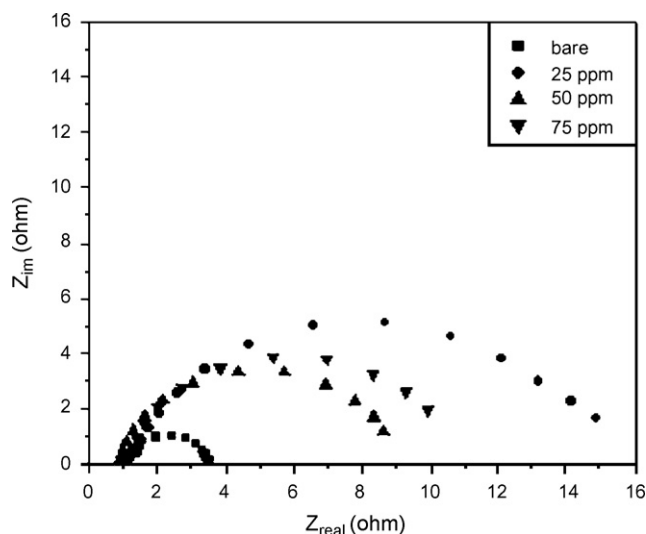


Fig. 8. Corrosion Impedance spectra recorded for MS/acid rain-containing PASM solution prepared by PD method at 25 ppm, 50 ppm and 75 ppm.

which is due to charge separation at metal/electrolyte interfaces. The impedance parameters calculated for mild steel/acid rain in polymer solution are given in Table 4.

The R_{ct} values obtained for various polymer concentrations were relatively high with respect to those observed for bare mild steel. This increase is related to the lowering of the charge transfer rate between the metal and the solution. The charge transfer reactions are known to take place at the metal/polymer solution interfaces. Consequently, the build up of protective passive layers and the effective barrier behavior of polymer film can explain the high R_{ct} values of inhibited mild steel.

The catalytic feature of polymer film is possible with ion diffusion processes taking place through the pores of the coating on the metal surface. However, the diffusion rate of ions depends on the porous structure of polymer film at the bottom of the pores which dissolves at some rate and hence the polymer film is reduced at the metal/polymer interface. These electrochemical reactions provide the formation of protective ferric oxide layers on the metal surface. It is well known for a real condenser that electrons control the charge distribution on both plates. However, some metals like iron do not behave as a real condenser. On the metal side of the double layer, electrons control the charge distribution whereas on the solution side it is controlled by ions. The double layer capaci-

Table 4
Impedance parameters of mild steel in acid rain for PASM

Polymer concentration (ppm)	Charge transfer resistance R_{ct} (Ω)	Double layer capacitance C_{dl} (μF)	Inhibition efficiency (%)
Bare	3.532	608.5	–
25	8.616	316.9	65.82
50	9.925	276.4	79.8
75	14.825	68.3	86.01

tance values, which were relatively low, proved being a steady oxide layer.

The impedance parameters of the corrosion behavior of PASM solutions on mild steel in acid rain can be summarized as follows:

1. High R_{ct} and low capacitance C_{dl} values suggest that PASM copolymer solution exhibits corrosion inhibition behavior on mild steel.
2. The corrosion inhibition efficiency for mild steel in acid rain PASM solution increases with the increase of PASM concentration from 25 ppm to 75 ppm.

4. Summary

The ability to copolymerize metanilic acid with anisidine has been potentiodynamically examined with monomer ratio of 1:3 on mild steel. The impedance parameters of PASM on mild steel substrate have been found to depend on the applied potential used for the deposition of the electrode. The application of copolymer solution as corrosion inhibitor was studied by using polarization techniques. It has been concluded that the PASM prepared by potentiodynamic method shows good corrosion control behavior.

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