



Chemical and Electrochemical Study of Effect of Soluble Sulfonated Polystyrene on Mild Steel Interface in Hydrochloric Acid Solution

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Highlights

- In various portions of these studies, the major focus was on corrosion solutions.
- Tafel plot and EIS examine the corrosion inhibition properties of sulfonated polystyrene.
- An Electrochemical and surface study supported the inhibitor properties.

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Abstract

The author has focused on the corrosive effect of 0.14% carbon steel in the occurrence of several amounts of soluble Sulfonated Polystyrene (SPS) and was found to be best efficient on soft iron exterior at 100ppm concentration in 0.5M hydrochloric acid assortment at 298K heat during 3h of time in this paper. The examination was performed by studying the weight loss of mild steel by varying different parameters like mixture concentration, time, and solution temperature. The efficiency of SPS was observed to rise with an increase of 91.90% of an inhibitor in the acid solution. The mechanism of physical adsorption was studied to the initiation and permitted dynamics for the reaction of altitude and extracted taking place towards the exterior of the iron sample in endothermic, impulsive and dependable through the Langmuir isotherm adsorption. Anodic and cathodic both type of nature of soluble SPS was studied using the potentiodynamic polarization method. The AFM analysis was used to do the surface and protective film analysis and under varied settings, SPS polymer inhibitor proven to be more suited for iron metal exterior.

1. INTRODUCTION

The economic study states that corrosion is leading a huge harmful effect on the development of countries as well as to the socioeconomic life of the society [1]. Oil pipes, bridges, vehicles, boilers etc. are facing a big challenge to avoid corrosion effect and decrease life of product. Industries of modern era's focus on belligerent acids for the use of routinely activities like acid pickling, cleansing, descaling, etc. which decomposes steel surface and fetches worsening of steel and its concerned properties [2,3]. The explosion of metal in the environment and coordination with the electrolyte environment the anodic reaction takes place to form rust by which the loss of metal forms by ion and free electrons reaction. A cathodic reaction is created to form an oxide film by conduction of electrons [4–6]. In the electrolyte that forms hydroxyl ions that respond to the ferrous ions formed by the anodic reaction, the dissolved oxygen is presented and forms ferrous hydroxide, which is then converted into a hydrated oxide generally referred to as 'rust'. The anodic area is blocked completely by this rust due to its porosity, and allows the rust to react deeply and spread to the anodic area in the metal which breaks the surface oxide film [7,8]. Off and on that the pH of the arrangement in interaction with the mild steel is low, as would be the situation in the event that a weaken corrosive is utilized, at that point the surface oxide film will be eliminated and the cathodic response will be unique. Hydrogen gases are going to be freed as continuous disintegration of the steel happens. With oxidizing acids, varied interchange electrode responses could happen. The anodic reaction in all the instances of corrosion cannot occur in isolation from the cathodic reaction. In addition, if any response can be reduced or avoided, a little or no corrosion can occur [9]. To keep away the material from such a movement numerous substance mixtures has been discovered viable and efficient strategy either the natural or inorganic mixtures commonly known as corrosion inhibitors [10]. The mixture which contains pi-electrons framework or particles is by all account the better choice for corrosion inhibitor for metals [11,12].

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Scientists find most of the natural, pharmaceutical and polymeric materials etc. in a calm condition mostly as noble reducing agent of corrosion on metals. Water soluble polymers has been extensively tested in many ways and have found that their high surface coverage area has strong absorption ability towards metal exterior and effectively protect the iron from corrosion [13].

The previous studies has focused on the characteristics and properties of several linear insulated water soluble corrosion inhibitors to be the best suited for the structure of metals and found most attentions in recent studies [14]. The ability of a good substance to serve as an inhibitor is determined by its ability to absorb on the work piece, i.e., a good inhibitor covers and protects surface of the metal specimen that allows water molecules to flow through. Good corrosion inhibitor states its inherent properties like stability, cost effectiveness, environmental issues and comparatively high efficiency of inhibition at minimum concentration in the solution [15]. The primary governing factors influencing the corrosive environment prohibitive presentation of those same polymeric mixtures affecting metal consumption in various destructive situations have been discussed. It has also been discovered from the past studies while the plant concentrates and oils show corrosion efficiency up to 98% [16,17], and shows that plant concentrates and oils are compelling inhibitors and can be effectively utilized at the modern level but the writing also uncovers that a wide scope of polymeric mixtures have been effectively examined and found to be more effective as compared to others [18,19], as potential inhibitors of corrosive environment in a dynamic media. Water soluble polymers like Polyvinyl alcohol, Polyacrylic acid, Poly(aniline-formaldehyde), Poly(o-toluedine-formaldehyde), Poly(p-chloroanilnie-formaldehyde), Hexahydro-1,3,5-triphenyl-s-triazine, Hexahydro-1,3,5-p-methoxyphenyl-s-triazine 3-anilinomethylpropionate and many more have been reported to be best suited inhibitor in their individual class for metals [20–27]. It was concluded the advantages of linear ionic polymer to be much better used over crossed linked polymers because of their solubility in water and ion exchange properties.

2. MATERIAL METHOD

All the corrosion studies like emaciation of metal and with the interconversion of chemical and electrical energy examination were performed on cold rolled mild steel metal strip of 10cm² surface area with thickness of 0.025cm, having structure (wt.%): 0.03% Phosphorus, 0.20% Copper, 0.35% Manganese, 0.17% Silicon, 0.025% Sulphur, 0.14% Carbon and rest iron [26,28]. An emery paper of grade 600 to 1200 mesh in⁻¹ was used to graze the additional Fe and polish the metal as like mirror finish [29].

The solubility of SPS [30] is achieved by the displacement of sodium ions by addition of hard water to Ca and Mg from separation from sulfonated group, which forms a softened sodium ion [31]. Using the dilution formula, the acid was prepared by the sum of acid used to deduce the volume get a solution ready [32]. The SPS polymer inhibitor in different concentration was diluted in the 0.5M HCl solution for analytical reagents with distilled water [33]. A solution of acid for 0.5M HCl of AR group and SPS of Merck India has been used with various concentrations at submerged mild steel area. The test bed was prepared by the methods stated in previous research paper [26, 34]. SPS has been tested and reviewed in the paper and has been used as primary inhibitor in this research article.

2.1. Experimental Setup

According to the weight loss method, a 10cm² surface zone of 0.14% carbon steel was immersed at 35°C with ± 1 °C heat tolerance every time in 0.5M HCl for 3h term in triplicate manner to find the average weight loss of each strip, using shimadzu balance, model AY62, for varying inhibitor value in combination with acid, whereas, mathematical relation existed established to report effectiveness of SPS inhibition on specimen surface in percentage, effective area (θ) and decay value (mmpy) in acidic medium for specimen has been reported somewhere [26, 35]. The adhesion of molecules and ions, to study the adsorption study of SPS on metal strip surface has been reported somewhere else [35] finding the natural, electrical potential shift in the characteristic of the solution interface utilizing several forms of isotherms [36]. The inhibitor concentration (C_{inh}), acidic medium adsorption constant (K_{ads}), and surface coverage values (θ), has been reported in the formula reported by Langmuir adsorption isotherm and fetched the value in the table using the Equation (1)

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}. \quad (1)$$

To examine the electrochemical potentiodynamic effects on the mild steel surface, a computer controlled Potentiostat / galvanostat instruments of model 1010E make Gamry instruments Inc. USA [11,37], were arranged with a mild steel strip of 1cm² of the exposed portion serves as the working probe, while calomel serves as an auxiliary probe and platinum foil serves as the reference probe, all has been prepared with surface cleaning method [38,39] for a three electrode assembly setup and arranged in a compartment for electrochemical examination of corrosion on mild steel surface. After steady state for further examinations, the tafel and linear polarization resistance, as well as differential thermal analysis, were reported for corrosion potential (E_{corr}), anodic (β_a) and cathodic (β_c) tafel slopes, and corrosion current density (I_{corr}) at -0.25V to +0.25V with an average scan rate of 0.5 mV/sec [26,40,41].

Polarization resistance (R_p) have been carried out at -0.20 mV to +0.20 mV with an average scan rate of 0.125 mV/sec after the steady state and can be found by the relation between working electrode surface area (A), and potential change dE and di using Equation (6), whereas IE% has been reported with and without inhibitor, using the equation reported by researchers [27,42,43]. The basic electrochemical impedance parameter like solution resistance (R_s), admittance parameter (Y_o), total number of parts (n), resistance to charges transfers (R_{ct}), and double electric layer capacitance (C_{dl}) be located to calculate the adhesion of atoms in metal and acid grains interface due to the potential difference between solution and electrode at corrosion state Using the equation [44,45]. Protective layer thicknesses (d) with double coating conductance (C_{dl}) are calculated using the preventive structure's relative permittivity (ϵ) and free space capacitance (ϵ_o) [32,46]

$$C_{dl} = (Y_o \cdot R_t^{1-n})^{1/n} \quad (2)$$

$$C_{dl} = \frac{\epsilon \epsilon_o}{d}. \quad (3)$$

The frequency spectrum from 100kHz to 0.01Hz was studied using an AC pulse with a 10mV amplitude. The dimension of the Nyquist plots was used to compute R_{ct} values [47].

AFM has been used by several researchers to identify a wide range of mechanical, electrical and magnetic and optical spectroscopic properties of specimen such as adhesion, rigidity, friction, dissipation, capacitance, electrostatic forces, mechanism of action, electrical current etc. [48,49]. AFM was used on worked samples to evaluate the superficial properties of mild steel specimens.

3. RESULTS AND DISCUSSIONS

3.1. Weight Loss Studies

Weight loss studies have been conducted and its data with % inhibition efficiency and corrosion rate is reported in Table 1. From the Table 1 it is evident that the inhibition efficiency of the mixture escalates from 30.68 % to 91.90% and corrosion rate decreases from 30.15 mmpy to 2.44 mmpy, at the same time when adding more soluble polystyrene from zero ppm to 100ppm in mixture. Trend of the increase in the inhibition efficiency is reported in the Figure 1. The rate of increase in inhibitor effectiveness elucidates the inhibitor particle's adsorption mostly on steel surface that comes into contact with the solution. At 100 ppm of adsorption the inhibitor prompting expanded the hindrance effectiveness as compared to zero ppm. This effect can be clarified depending upon interaction of metal and inhibitor particle to study the adsorption on the surface. Overall, inhibitor atoms slow down specimen disintegration by framing and isolating a special covering adsorbing towards the base metal from the corrosive fluid [26,35, 50]. Any electron ion pair found in the benzene ring in the form of pi- electrons produces the strength of chemical binding. It can be achieved by the corrosion suppression ability of inhibitor molecule acting at interface [36,50].

It was also observed that the different parameters of experiment likes duration of immersion time of metal strip in solution from 3h to 8h is reported in Figure 2(a). It is evident from the Figure 2(a) that by increasing the time inhibition efficiency decreases, that suggest that the adsorption of the molecule on metal surface is decreases due course of increase in the exposure time of the metal surface in the acidic environment. This may leads to the desorption of the molecule from the surface of the metal due to destruction of the inhibitor film. Destructions of the metal film are due to the effect of the acid agitation and the degradation of the inhibitor molecule in longer exposure in the acidic media. Therefore this inhibitor is found best suited for 3h immersion time [26, 51].

Table 1. Impact of variable inhibitor concentration in aqueous condition on mild steel surface

C_{inh} (in ppm)	AWL (in mg)	IE (%)	CR (in mmpy)
Nil	81.05	-	30.15
15	56.19	30.68	20.90
25	37.60	53.61	13.99
50	20.85	74.28	7.76
75	7.17	91.16	2.67
100	6.57	91.90	2.44

C_{inh} : Inhibitor Concentration

AWL: Average Weight Loss

IE: Inhibitor Efficiency

CR: Corrosion Rate

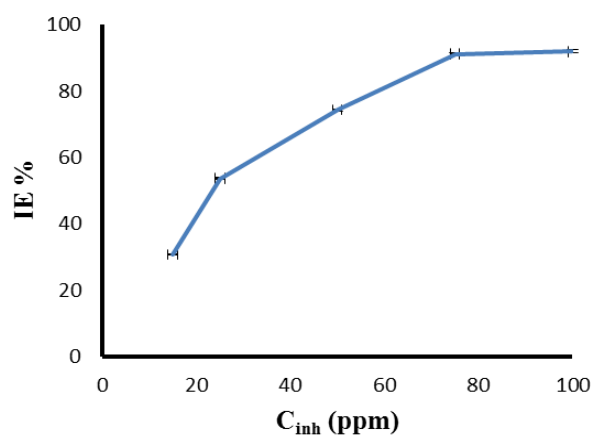


Figure 1. Impact of inhibitor concentration on mild steel in 0.5M HCl solution at 30°C for 3h duration

Studies have also been done on the various temperature ranges from 298K to 328K variation is reported in Figure 2(b). Decrease in the inhibition efficiency by increase in the temperature range suggested [44, 51] that the adsorption of the inhibitor follows physical adsorption mechanism. It is best suited inhibitor at lower temperature ranges. Similarly acidic concentration has been varied from 0.5M to 2M in constant 100 ppm inhibitor concentration reported in Figure 2(c) and found best suited for their functioning is at 0.5M concentration of the acid.

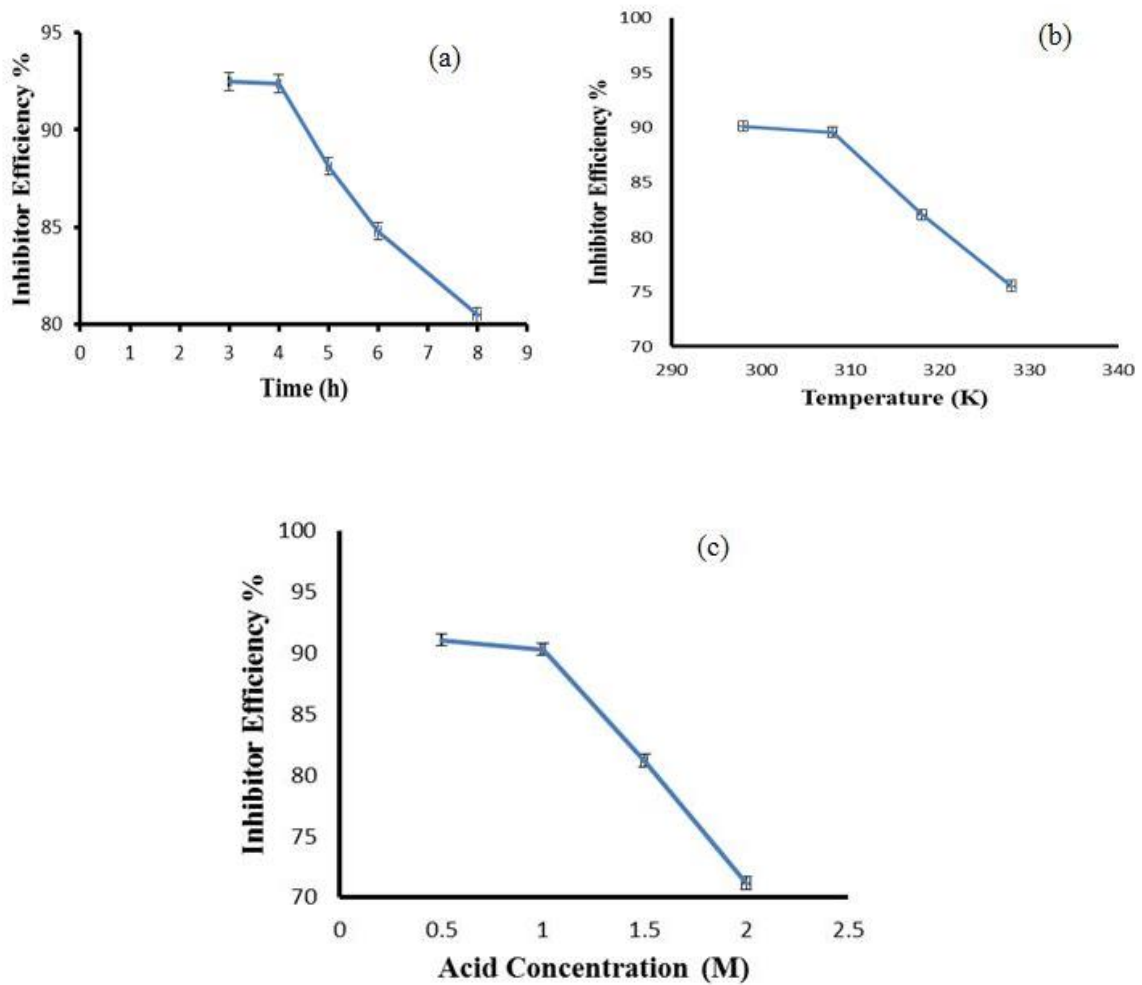


Figure 2. At constant inhibitor concentration 100ppm the individual variable parameter(s) for weight loss study like (a) Duration, (b) Temperature (c) Acidic concentration

3.2. Adsorption Studies

Various isotherms were tested with the parameters calculated from the weight loss data and it is found that the Langmuir isotherm is best suited isotherm for the adsorption for SPS inhibitor for mild steel surface at 100ppm concentration of inhibitor at 0.5M HCl at 35°C for 3h duration reported in Figure 3. It has been found after the examination of the Figure 3 that the value of regression coefficient (R^2) is about to be unity, represents the finest definition of adsorption activity by isothermal adsorption by Langmuir [26,42,51].

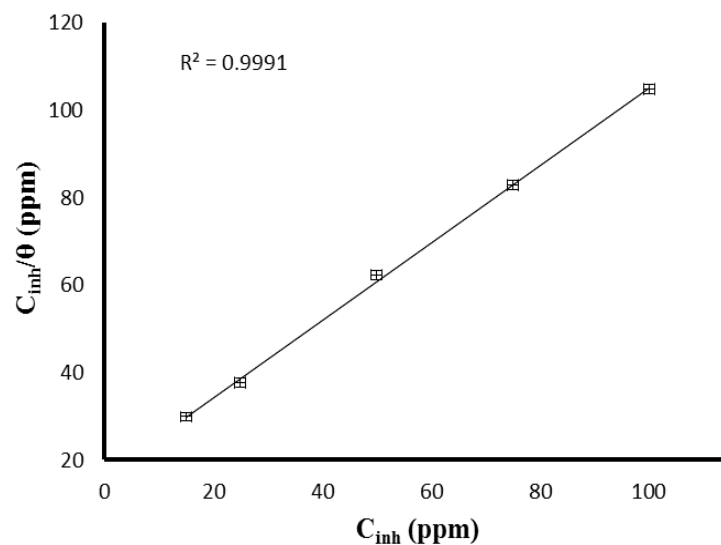


Figure 3. Adsorption of soluble SPS polymer inhibitor molecules into 0.5 M HCl solution on a mild steel surface using Langmuir's adsorption chart with deviation bar

3.3. Electrochemical Impedances (EIS)

For mild steel corrosion, the impedance range observed in 0.5 M SPS is necessary for an arc representing the interface between the iron surface and the corrosive environment. This occurrence is best described by the $-R$ (CR) model. As seen in Figure 4, the semicircle in impedance plots is made up of depressed semicircles with the center below the real axis. As the concentration of inhibitor increases, the semicircle expands, showing that charge transfer is the dominant regulatory factor in mild steel corrosion. The plots demonstrate that as the concentration of the inhibitor grew, so did the impedance of the inhibited solution.

Table 2. Values for EIS for 0.14%C steel with varying inhibitor amount of SPS on corrosion rates 0.5M hydrochloric acid solution

C_{inh} (ppm)	R_s (Ω cm ²)	R_p (Ω cm ²)	Y_o (μ F cm ⁻²)	n	C_{dl} (μ F cm ⁻²)	IE (%)
Blank	1.23	8.3	1181.5	0.858	55	-
25	1.13	68.7	321.0	0.829	51	87.9
50	1.05	82.5	270.5	0.824	48	89.9
75	0.90	102.1	211.4	0.818	47	91.9
100	0.98	121.7	121.3	0.809	45	93.1

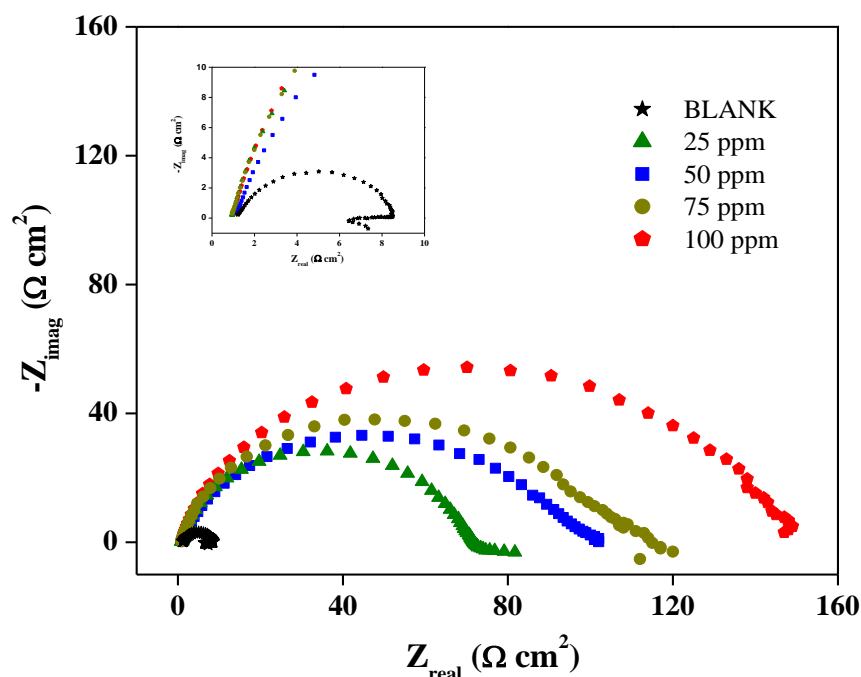


Figure 4. Nyquist plot of impedance spectra of corrosion inhibition process 0.5 M hydrochloric acid solution on mild steel surface in the absence and presence of various concentration of SPS

The experimental effects of EIS tests of mild steel corrosion in 0.5 M SPS in the variation of an inhibitor has been described in Table 2. The amount of charge transfer resistance (R_{ct}) increases with increase in the inhibitor concentration. Reduction the increase in the charge transfer resistance suggested that the process of corrosion is hindered due to increase in corrosion inhibitor. Double layer capacitance (C_{dl}) values decreases suggesting the decrease in flow of corrosion current on the metal surface, consequence of that the corrosion decreases and inhibition of metal increases.

3.4. Polarization Measurements

According to Table 3, the linear polarization curve has the corrosion potential increment with increase in the temperature and the inhibitor efficiency is increase upto 90.9% by increase in the concentration of inhibitor. Tafel polarization data was utilized to calculate corrosion potential (E_{corr}), corrosion current density (I_{corr}), and cathodic and anodic tafel slopes (β_c and β_a). The results revealed that raising the concentration of the inhibitor decreases the corrosion current with the increase in the inhibitor concentration.

Table 3. The characteristics of linear and tafeltest on 0.14%C steel in varying SPS amount in 0.5M HCl at 35°C for 3h

C_{inh} (ppm)	Tafel Polarization data					Linear Polarization data	
	I_{corr} ($\mu A cm^{-2}$)	$-E_{corr}$ (mV vs SCE)	β_c (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	IE (%)	R_p (Ωcm^2)	IE (%)
Blank	2140	469	150	75	-	20.1	-
25	590	476	146	69	72.4	105	80.9
50	425	461	139	71	80.1	168	88.0
75	330	465	153	68	84.5	190	89.4
100	235	467	151	67	89.0	221	90.9

It is found in Figure 4 that it might be regarded to adjust the anodic and cathodic panels of the tafel by adding SPS to corrosive media. During the path changes, both cathodic and anodic reactions were shown to be affected by the inhibitor. However, the impact is more prominent compared to that in anodic polarization plots in cathodic polarization plots [42, 51]. Since the measurements β_c and β_a in Table 3 change with an increase in the inhibitor concentration, a high β_c value indicates that the cathodic reaction is more delayed than the anodic [52].

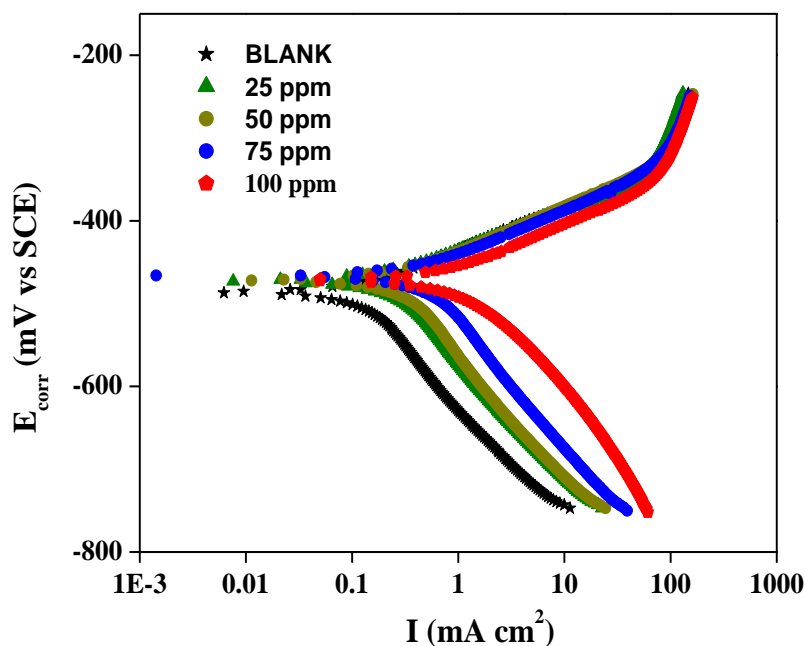


Figure 5. Potentiodynamic polarisation curves of mild steel in the absence and presence of inhibitors submerged in the 0.5M SPS solution

Figure 5 further shows that, in comparison to the anodic curves, the presence of the inhibitor drive the cathodic curves to a greater degree towards the lower current density. E_{corr} advantage shifts to the more damaging side when the concentration of the inhibitor rises. The adsorption of the inhibitor molecule to the metal surface reduces the rate of hydrogen evolution process on the metal specimen surface, resulting in these advantages [53]. As a chemical based on transition from the E_{corr} value a cathodic and anodic type inhibitor has been found. When E_{corr} is moved by more than 85 mV from null to cathode, the inhibitor is classed as a mixed-type inhibitor. In our study, the major change in E_{corr} value was 6 mV, indicating that the inhibitor is a mixed and more anodic shape that has no influence on the response mechanism. The action of the inhibition is caused by the fundamental blocking of active sites, which diminishes the surface area of the corroding metal [48,54].

3.5. AFM Studies

In three separate cases, AFM was used to test the external properties of 0.14% C steel materials, as seen in Figure 6 (a), (b) and (c) [55]. Figure 6(a) displays the surface morphology of the bare mild steel polished surface, while 6(b) and 6(c) reflect the MS specimen without and with an inhibitor, respectively. Due to the interaction of 0.5 M HCl, the rough surface of the MS sample was observed in Figure 6(b), whereas Figure 6(c) provides a much smoother surface due to the inclusion of a SPS polymer inhibitor in the mixture that adsorbs on metal samples and forms a decreased rate of corrosion on the mild steel surface and acid interface.

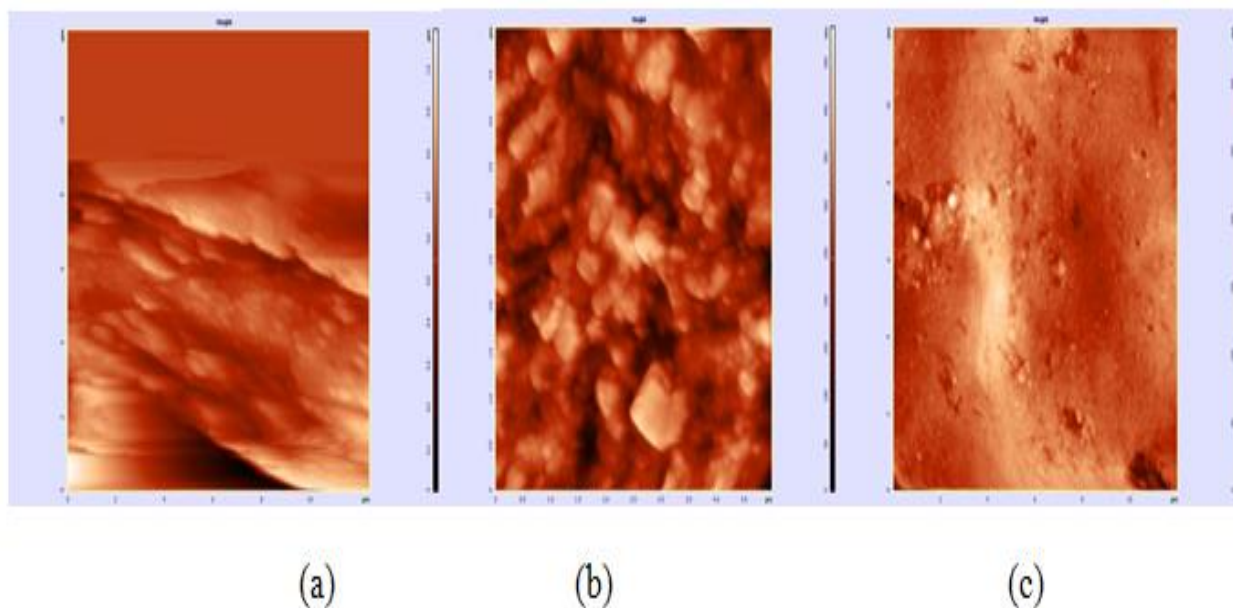


Figure 6. Surface morphological examination of the mild steel sample by atomic force microscopy where, (a) Polished sample (b) Test immersed in 0.5 M HCl without inhibitor for 3 h (c) Test immersed in 0.5 M HCl with 100 ppm of sulphonated polystyrene inhibitor for 3 hours [55]

4. CONCLUSION

Influence of the SPS on mild steel corrosion in acidic environment were studied and it is found that the increasing concentration of the inhibitor from 10 to 100 ppm leads the increase in the inhibition efficiency in the acidic environment and the decrease in the corrosion rate of the mild steel. Optimum inhibition efficiency is observed at 100 ppm concentration of the inhibitor concentration.

The polarization experiments shows that the decrease in the corrosion current (I_{corr}) with the increase in inhibitor concentration suggests that the inhibition efficiency increases and corrosion rate decreases. EIS studies were also in good agreement with the weight loss and polarization studies. It is also found with studies that it is a mixed type of inhibitor and regulated by a method of charge transfer and form adsorbed uniformly on the surface. AFM studies show that the roughness of the surface decreased significantly by the use of the inhibitor molecule.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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