

Research Article

Influence of Polythiophene-p-Toluenesulphonic Acid on Corrosion Inhibition of Carbon Steel in Acid Medium

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ABSTRACT

The inhibitive action of chemically synthesized polythiophene-p-toluenesulphonic acid (PTh-p-TSA) on carbon steel in 1N HCl was studied using chemical and electrochemical techniques. Potentiodynamic polarization studies revealed that PTh-p-TSA was mixed type inhibitor and exhibited around 92.5% inhibition efficiency at the concentration of 700 ppm. The effect of temperatures on the corrosion behavior of carbon steel was studied in the temperature ranging from 30°C to 90°C for 1N HCl at the optimum concentration of 700 ppm. The adsorption behavior of this polymer on carbon steel surface in 1N HCl was found to obey Langmuir adsorption isotherm. Thermodynamic parameters including the free energy of adsorption, activation energy, enthalpy, entropy and heat of adsorption were also calculated. The protective film formed on the metal surface (carbon steel) by the adsorption of PTh-p-TSA was confirmed by SEM studies.

Keywords: Polythiophene-p-toluenesulphonic acid, Polymeric inhibitors, Carbon steel.

INTRODUCTION

Acid solutions are widely used in industries for picking, cleaning, descaling etc. because of their aggressiveness. To control the rate of dissolution of metals, inhibitors are used. The compounds containing nitrogen, sulphur and oxygen have been reported as inhibitors¹. The presence of functional groups such as =NH, -N=N-, -CHO, R-OH, etc. in the inhibitor molecules and also the π -electrons in their structures are found to influence the adsorption of the inhibitor molecule over corroding metal surface²⁻⁴. Recent days, polymers and conducting polymers have been in use as corrosion inhibitors in industries, because of their wide range of applications and economics⁵⁻⁷. In the present work, the inhibitive behavior of polythiophene-p-toluenesulphonic acid on carbon steel in 1N HCl solution has been studied.

Experimental

Material Preparation

Carbon steel strips of size 4.5cm×2cm×0.2cm containing 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and the remainder Fe were used for weight loss and gasometric methods. For electrochemical studies, carbon steel strips of the same composition coated with lacquer with an exposed area of 1cm² were used. Mild steel strips were polished mechanically with emery papers of 1/0 to 4/0 grades. They were subsequently degreased with trichloroethylene before use. Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solutions for all experiments.

Synthesis of PTh-p-TSA Nanopowder

Polythiophene-p-toluenesulphonic acid (PTh-p-TSA) nanopowder was synthesized by surfactant assisted dilute polymerization method using cationic surfactant such as cetyltrimethylammonium bromide (CTAB). In

this method, thiophene monomer (0.1 mol) was added drop by drop into 20 ml of chloroform containing 0.014 mol of surfactant (CTAB) and 0.4 mol of anhydrous FeCl_3 and 0.1 mol of *p*-toluenesulphonic acid under stirred condition. The ratio of [monomer] / [surfactant] was kept about 7/1⁸. The polymerization process was identified by the change in the colour of reaction mixture into brown. The polymerization process was given continuous stirring for 24 hr at 30°C. The dark-brown precipitate

of polythiophene-*p*-toluenesulphonic acid was collected by the filtration of reaction mixture and washed with distilled water and methanol until colourless filtrate was obtained. The obtained PTh-*p*-TSA nanopowder was dried in vacuum oven at 80°C for 6 hr. The reaction for PTh-*p*-TSA synthesis is shown in Fig.1.

The prepared PTh-*p*-TSA powder was confirmed by FTIR spectral studies and its particles size was measured by SEM studies and it was found to be < 40 nm (Fig.2).

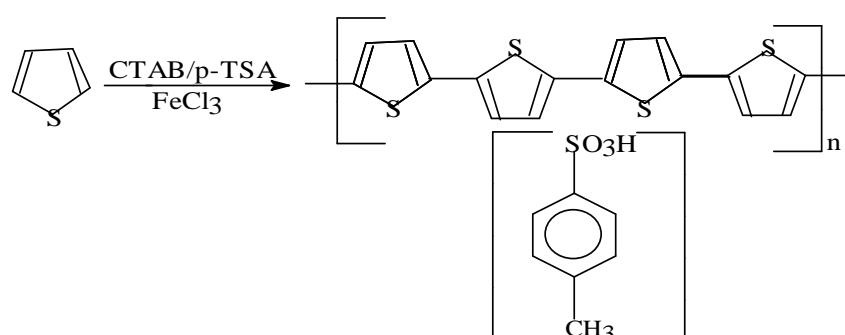


Fig.1: Synthesis of PTh-*p*-TSA Nanopowder

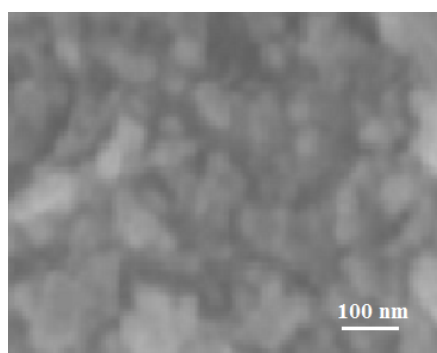


Fig.2: SEM image of PTh-*p*-TSA Nanopowder

Corrosion Inhibitor Studies Weight Loss Measurements

Weight loss measurements were carried out as described elsewhere⁹. Carbon steel specimens were immersed in 100ml of inhibited and uninhibited 1N HCl solution for 3 hours at 30°C. The corrosion rate (mmpy) and the inhibition efficiency were calculated using the following equations;

$$\text{Corrosion rate (mmpy)} = KW/ATD$$

Where, $K = 8.76 \times 10^4$ (constant),
 W =weight loss in g, A = area in square cm,
 T = time in hrs and D = density in gm /
 cu.cm (7.88).

$$\text{Inhibition Efficiency (\%)} = \frac{W_B - W_I}{W_B} \times 100$$

Where, W_B and W_I are weight loss per unit time in the absence and presence of PTh-*p*-TSA.

Effect of Immersion Time

To know the stability of inhibitors for a longer duration, the effect of immersion time on corrosion of carbon steel in 1N HCl was also carried out at various immersion times from 3 to 24 hours at an optimum concentration of PTh-p-TSA at 30°C. From the initial and final weight of the specimen, the loss in weight was calculated at various immersion times.

Determination of Surface Coverage

The degree of surface coverage (θ) was calculated from the weight loss measurement results using the formula¹⁰;

$$\text{Surface coverage } (\theta) = \frac{W_B - W_I}{W_B}$$

Where, W_B is the weight loss in the absence of PTh-p-TSA, W_I is the weight loss in the presence of PTh-p-TSA. The data were tested graphically for fitting a suitable isotherm.

Potentiodynamic polarization studies

Potentiodynamic polarization measurements were carried out using EG & G PAR - Potentiostat /Galvanostat (Model -173) analyzer a universal programmer in a conventional three-electrode glass cell. A platinum foil of surface area 2cm² was used as the auxiliary electrode and a saturated calomel electrode as the reference electrode. Both anodic and cathodic polarization curves were recorded in the absence and presence of an optimum concentration of PTh-p-TSA from a cathodic to an anodic potential of ± 250 mV (vs SCE) at a sweep rate of 1mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula;

$$\text{IE (\%)} = \frac{I_{\text{Corr}} - I_{\text{Corr}}^*}{I_{\text{Corr}}} \times 100$$

Where, I_{Corr} and I_{Corr}^* are corrosion current in the absence and presence of PTh-p-TSA.

Electrochemical Impedance Studies

The electrochemical AC-impedance measurements were performed using EG & G Electrochemical impedance analyzer (Model – 6310) with M38 software as described earlier¹¹. Experiments were carried out at the open circuit potential for the frequency range of 100 kHz to 10 MHz. A plot of Z' vs Z'' were made. From the plots, the charge transfer resistance (R_t) were calculated and the double layer capacitance (C_{dl}) were then calculated using the equation⁹.

$$C_{dl} = 1 / 2\pi f_{\text{max}} R_t$$

The experiments were carried out in the absence and presence of an optimum concentration of the inhibitor. The percentage of inhibition efficiency was calculated using the equation;

$$\text{IE (\%)} = \frac{R_t^* - R_t}{R_t^*} \times 100$$

Where, R_t^* and R_t are the charge transfer resistance in the presence and absence of PTh-p-TSA.

Effect of Temperatures

The effect of temperatures on the corrosion behaviour of carbon steel was studied by weight loss measurements at various temperatures ranging from 30 to 90°C in the absence and presence of an optimum concentration of PTh-p-TSA in 1N HCl solution for an immersion period of 3 hours.

Surface Examination Study

The carbon steel specimens were immersed in 1N HCl in the absence and presence of an optimum concentration of the inhibitor for 3 hour at 30°C. After 3 hour, the specimens were taken out, dried and kept in desiccators. The protective film formed on the surface of carbon steel was confirmed by SEM studies with the magnification of 1000X.

RESULTS AND DISCUSSION

Weight loss method

The weight loss studies was performed with various concentrations of PTh-p-TSA ranging from 100 - 900ppm, to follow the

influence of various concentrations of the inhibitor and immersion time on the corrosion inhibition of PTh-p-TSA on carbon steel in 1N HCl at 30°C for a period of 3 hours. The corrosion parameters obtained from weight loss measurements for carbon steel in 1N HCl containing various concentrations of PTh-p-TSA are listed in Table- 1. It was found that with the rise in concentration of PTh-p-TSA from 100 to 700 ppm in 1N HCl, the corrosion rate of carbon steel decreased while the inhibition efficiency increased from 74.2 % to 92.5 % upto 700ppm and then decreased to 90.4% at the

concentration of 900ppm. Hence, the optimum concentration was found to be 700 ppm with a highest inhibition efficiency of about 92.5%.

The effect of immersion time from 3 hours to 24 hours was also studied. The effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of an optimum concentration (700ppm) of PTh-p-TSA is shown in Table-2 (Fig.3). It shows that the immersion time increases, the inhibition efficiency was found to be decreased from 92.6% to 90.1% for carbon steel in 1N HCl solution.

Table 1: Corrosion parameters obtained from weight loss measurements for carbon steel in 1N HCl containing an optimum concentration of PTh-p-TSA

Conc. of PTh-p-TSA (ppm)	Weigh Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	0.2860	118.16	---	---
100	0.0738	30.48	74.2	0.74
300	0.0589	24.20	79.5	0.80
500	0.0383	15.82	86.6	0.87
700	0.0212	8.86	92.5	0.93
900	0.0275	11.36	90.4	0.90

Table 2: Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in the presence of an optimum conc. (700ppm) of PTh-p-TSA

System	Inhibition Efficiency (%)							
	Time (h)							
	3	6	9	12	15	18	21	24
700 ppm of PTh-p-TSA	92.6	92.4	92.2	91.8	91.4	91.0	90.5	90.1

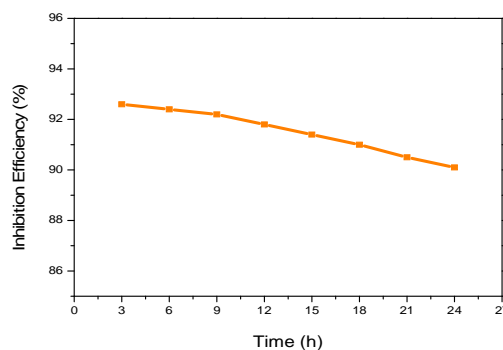


Fig. 3: Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of an optimum concentration (700ppm) of PTh-p-TSA

Potentiodynamic Polarization Method

The Potentiodynamic polarization measurements was made to evaluate the corrosion current, corrosion potential and Tafel slopes. The Potentiodynamic polarization parameters for carbon steel in 1N HCl in the absence and presence of an optimum concentration of PTh-p-TSA is given in Table-4 and the polarization curves for carbon steel in 1N HCl solution in the absence and presence of an optimum concentration of PTh-p-TSA is shown in Fig.4. It can be seen from the table that the corrosion potential was not shifted significantly in presence of the inhibitor suggesting that the PTh-p-TSA control both anodic and cathodic reactions to inhibit the corrosion of carbon steel by blocking active sites on the carbon steel

surface¹². Hence, it is inferred that the inhibition action is of mixed type. Table-4 shows that the corrosion current is markedly decreased from 3.68 mA/cm² to 0.25 mA/cm², upon the addition of PTh-p-TSA. The extent of its decrease increased with the addition of an optimum concentration (700ppm) of PTh-p-TSA. This behaviour reflects the ability of PTh-p-TSA to inhibit the corrosion of carbon steel in 1N HCl solution. The numerical values of both anodic and cathodic Tafel slopes decreased as the concentration of PTh-p-TSA increased. It was observed that with increase in concentration of PTh-p-TSA from 100 to 700 ppm, the maximum inhibition efficiency of 93.2% was observed at the optimum concentration of 700ppm.

Table 4: Potentiodynamic polarization parameters for carbon steel in 1N HCl in the absence and presence of an optimum concentration of PTh-p-TSA

Conc. of PTh-p-TSA (ppm)	E_{corr} (V vs SCE)	I_{corr} (mA/cm ²)	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-488	3.68	84.4	102.2	---
700	-492	0.25	84.1	103.6	93.2

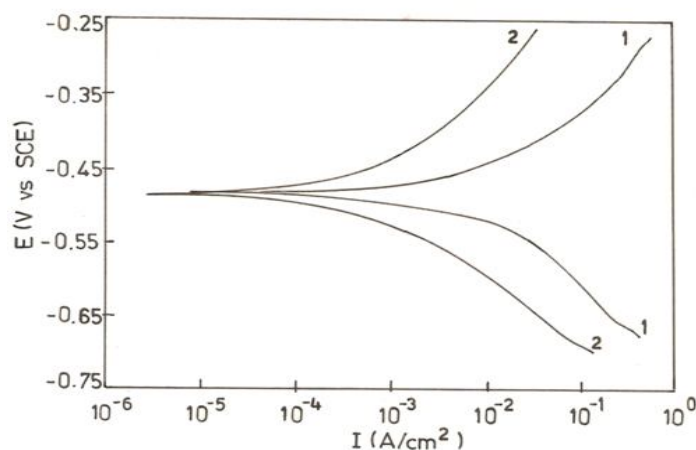


Fig. 4: Potentiodynamic polarization curves for carbon steel in 1N HCl solution in the absence and presence of an optimum conc. of PTh-p-TSA Blank (1) 700 ppm of PTh-p-TSA (2)

AC- Impedance Measurements

Impedance measurements were studied to evaluate the charge transfer resistance (R_t) and double layer capacitance (C_{dl}) and through these parameters the inhibition efficiency was calculated. Fig. 5

shows the Nyquist representation of impedance behaviour of carbon steel in 1N HCl solution in the absence and presence of an optimum concentration of PTh-p-TSA and the impedance parameters derived from these

investigations are given in Table 5. In fact, the presence of PTh-p-TSA enhanced the values of R_t in acidic solution. Impedance diagrams are almost semicircular appearance is due to the charge transfer processes. Deviations of

perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena¹³.

Table 5: Impedance parameters for the corrosion of carbon steel in 1N HCl in the absence and presence of an optimum concentration of PTh-p-TSA at 30°C

Conc. of PTh-CA (ppm)	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	Inhibition Efficiency (%)
Blank	20.2	5046	---
700	306.4	612	93.4

Double layer capacitance values are brought down to the maximum extent in the presence of inhibitor and the decrease in values of C_{dl} followed the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl} showed that the adsorption of this inhibitor took place on the carbon steel surface in acid solution. The increase in the value of R_t with the inhibitor concentration led to an increase in inhibition efficiency. The R_t value without inhibitor (blank) was found to be

20.2 $\Omega \text{ cm}^2$ and C_{dl} value was 5046 $\mu\text{F}/\text{cm}^2$. At the optimum concentration of 700 ppm, the R_t value of 306.4 $\Omega \text{ cm}^2$ and minimum C_{dl} value of 612 $\mu\text{F}/\text{cm}^2$ was obtained with a maximum inhibition efficiency of 93.4 %.

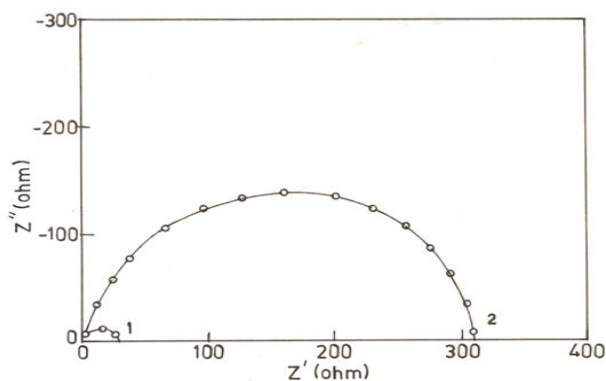


Fig. 5: Impedance diagrams for carbon steel in 1N HCl solution in the absence and presence of an optimum concentration of PTh-p-TSA (1) Blank 2) 700 ppm of PTh-p-TSA

Effect of Temperatures

The effect of temperatures on the corrosion behaviour of carbon steel was studied by weight loss measurements at various temperatures ranging from 30 to 90°C in the absence and presence of an optimum concentration of PTh-p-TSA (700

ppm) in 1N HCl solution. The corrosion rate and inhibition efficiencies with respect to temperatures for carbon steel in 1N HCl in presence of an optimum concentration of PTh-p-TSA is shown in Table-6. It can be seen from the table that the increase in corrosion rate was more pronounced with

the rise in temperature for the uninhibited acid solution than the inhibited solution suggesting that PTh-p-TSA adsorbed on the carbon steel surface at all temperatures studied. But, as the

temperature increased from 30°C to 90°C, the inhibition efficiency of PTh-p-TSA decreased from 92.5 to 84.2%.

Table 6: Corrosion of carbon steel in the absence and presence of an optimum concentration of PTh-p-TSA in 1N HCl at different temperatures obtained by weight loss method

System	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	118.16	---
	50	147.91	---
	70	186.21	---
	90	239.90	---
700 ppm of PTh-p-TSA	30	8.86	92.5
	50	13.79	90.6
	70	24.55	86.8
	90	41.61	84.7

Mechanism for the corrosion inhibition of PTh-p-TSA

The Arrhenius plot for carbon steel immersed in 1N HCl solution in the absence and presence of an optimum concentration (700ppm) of PTh-p-TSA is shown in Fig.6. The relationship between the temperature dependence on percentage inhibition efficiency of the inhibitor and the activation energy found in its presence can be classified into three groups according to temperature effects¹⁴⁻¹⁸.

1. Inhibitors whose inhibition efficiency decreases with increase in temperature, the value of apparent activation energy (E_a) is greater than that obtained in the uninhibited solution.
2. Inhibitors whose inhibition efficiency does not change with temperature variation, the apparent activation energy (E_a) does not change in the presence or absence of inhibitor.
3. Inhibitors whose inhibition efficiency increases with temperature increase, the value of apparent activation energy (E_a) for the corrosion process is smaller than that obtained in the uninhibited solution.

The calculated values of activation energy (E_a), enthalpy of adsorption (ΔH), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS) are shown in Table 7. The activation energy, E_a was found to be 10.95KJ mol⁻¹ for blank (1N HCl) and 23.95 KJ mol⁻¹ in the presence of PTh-p-TSA suggesting that the inhibition efficiency decreased with temperature variation.

The negative sign of free energy of adsorption indicates that the adsorption of PTh-p-TSA on carbon steel surface is a spontaneous process. In this study, the ΔG° values were in the range -17.35 KJ mol⁻¹ to -17.92 KJ mol⁻¹. As the values of free energy of adsorption were less than -20 KJ mol⁻¹ and hence the inhibition is due to physisorption^{19,20}. The positive values of enthalpy of adsorption (ΔH) show that the reaction is endothermic and the adsorption of the inhibitor on the metal surface takes place easily. Entropy of adsorption (ΔS) remains a positive value and this reflects the formation of stable layer of the inhibitor molecule on the carbon steel. Moreover, the positive value of entropy indicates that the reaction is said to be spontaneous and feasible. The inhibition action may be due to the presence of long π electrons of heterocyclic rings and lone pair of electrons of sulphur and sulphonic acid

groups present in PTh-p-TSA²¹. These molecules can adsorb on the carbon steel surface and make a barrier for charge and mass transfers leading to decrease the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal decreased. The formation of film layer essentially blocked

the dissolution of metal ions. The corrosion of carbon steel in 1N HCl solution is a heterogenous one, composed of anodic and cathodic reactions. The adsorption of various concentrations of PTh-p-TSA on the surface of carbon steel in 1N HCl followed Langmuir adsorption isotherm (Fig. 7).

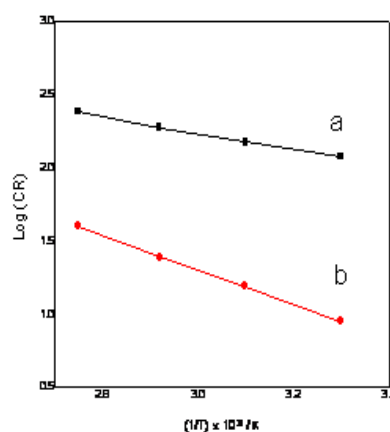


Fig. 6: Arrhenius plots for carbon steel immersed in 1N HCl solution in the absence and presence of an optimum concentration of PTh-p-TSA
a) Blank b) 700ppm of PTh-p-TSA

Table 7: Calculated values of activation energy (Ea), enthalpy of adsorption (ΔH), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS) for mild steel in the absence and presence of an optimum conc. of PTh-p-TSA in 1N HCl solution

System	Temp. (K)	Ea (KJ mol ⁻¹)	ΔG° (KJmol ⁻¹)	ΔH (KJmol ⁻¹)	ΔS (KJmol ⁻¹)
Blank	303	---	---	8.43	---
	323	9.14	---	8.26	---
	343	10.61	---	8.10	---
	363	13.11	---	7.93	---
700 ppm of PTh-p-TSA	303	---	-17.35	21.43	0.1280
	323	17.99	-17.86	21.26	0.1211
	343	26.56	-17.84	21.10	0.1135
	363	27.30	-17.92	20.93	0.1070

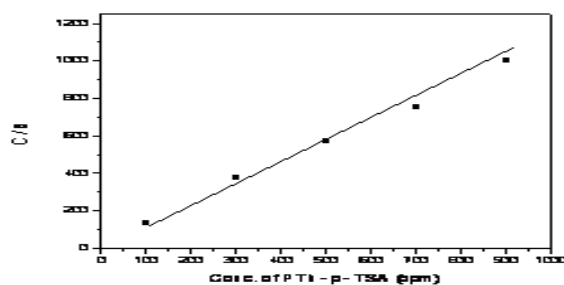


Fig. 7: Langmuir adsorption isotherm plot for the adsorption of various conc. of PTh-p-TSA on the surface of carbon steel in 1N HCl solution

3.6 Surface Analysis

The carbon steel specimens after immersion in 1N HCl solution for three hours at 30°C in the absence and presence of an optimum concentration (700ppm) of the PTh-p-TSA were taken out, dried and kept in desiccators. The protective film formed on the surface of carbon steel was confirmed by SEM studies is shown in Fig.8 (a & b).

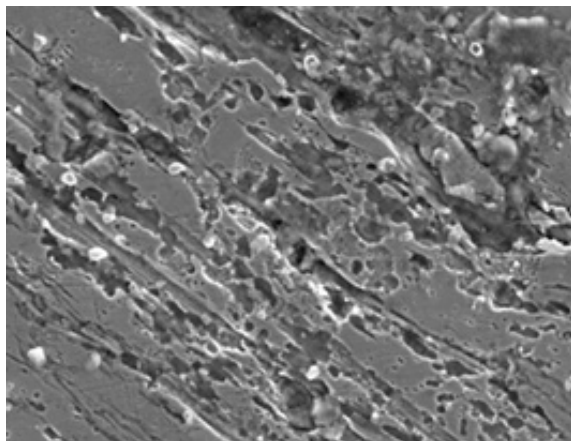


Fig. 8 (a): SEM Photograph of carbon steel immersed in 1N HCl solution (blank)

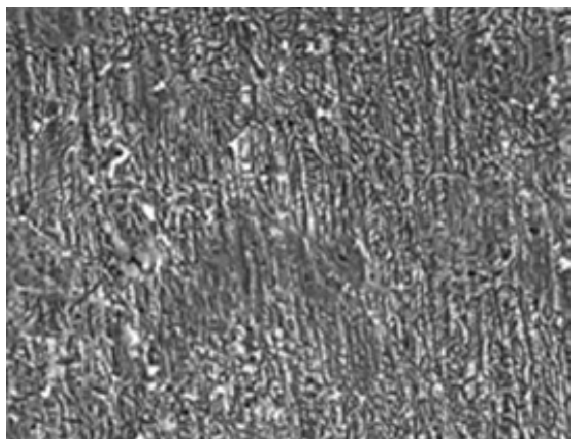


Fig. 8 (b): SEM Photograph of carbon steel immersed in 1N HCl containing an optimum concentration (700 ppm) of PTh-p-TSA

CONCLUSIONS

The polymer polythiophene-p-toluene sulphonic acid (PTH-p-TSA) is found to have a significant influence on corrosion inhibition of carbon steel in 1N HCl at a concentration of 700 ppm. PTh-p-TSA control both anodic and cathodic reactions by blocking the active sites of steel

surface and thus the inhibitor of mixed type. The adsorption of PTh- p-TSA on carbon steel surface in 1N HCl solution is found to obey Langmuir adsorption isotherm. The adsorption and the inhibition action of PTh-p-TSA on carbon steel are well evidenced by SEM studies.

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