



Polythiophene- β -Naphtholsulphonic acid: New and effective corrosion inhibitor for carbon steel in acid solution

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Abstract

New and effective polymeric inhibitor polythiophene- β -naphtholsulphonic acid (PTh- β -NSA) was prepared and used as corrosion inhibitors for carbon steel in 1N HCl solution using chemical and electrochemical methods. Results obtained from weight loss and gasometric methods were in good agreement with electrochemical methods. Potentiodynamic polarization measurements show that PTh- β -NSA was a mixed type inhibitor. 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 an optimum concentration of 700 ppm. The adsorption behavior of this polymer on carbon steel in 1N HCl was found to obey Langmuir adsorption isotherm. The effect of decrease in the hydrogen permeation current through the carbon steel surface was studied by the hydrogen permeation technique. The protective film formed on carbon steel by the adsorption of PTh- β -NSA was confirmed by SEM studies.

Key words: Polythiophene- β -naphtholsulphonic acid, corrosion inhibitors, carbon steel, hydrogen permeation studies, langmuir adsorption isotherm

Introduction

Acid solutions are widely used in industries for picking, cleaning of boilers, descaling and oil-well acidizing etc. To control the rate of undesirable base metal corrosion, corrosion inhibitors are employed¹⁻⁴. Research activities over a century have brought tremendous advances in the field of corrosion inhibitors. Hot acid solutions are generally used for removing mill scales from the metal surfaces in various industries at elevated temperatures such as 60°C in HCl solution. To minimize the percentage of metal loss during this process, various compounds such as acetylenic alcohols, indoles, thiourea derivatives, dithiazones, etc. are widely used⁵⁻¹⁰. Among these, thiourea and its derivatives were found in commercial formulations, but because of toxic nature their use is not safe. There is a great need to find a non-toxic replacement that is compatible with current industrial technologies. In the last two decades, there has been an increase in the use of polymeric compounds as corrosion inhibitors. Intrinsically, conducting polymers were tried as corrosion inhibitors¹¹.

The conducting polymers should offer better corrosion inhibition efficiency than simple organic compounds due to their inherent polar nature. The conducting polymers are rich in electrons due to the presence of long π -electron conjugations and hence, can effectively be adsorbed on the metallic surfaces¹². The literature reveals that a wide range of polymeric compounds have been successfully investigated as potential inhibitors for the corrosion of metals in aggressive media¹³. In

continuation of our quest for development of corrosion inhibitors with high inhibition efficiency, the present investigation aims at the utilization of PTh- β -NSA as corrosion inhibitor for carbon steel in 1N HCl solution and its corrosion inhibition performance has been studied using chemical and electrochemical methods, and their results are discussed.

Material and Methods

Material Preparation: The carbon steel strips of size 4.5cm \times 2cm \times 0.2 cm containing 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and the remaining 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- β -NSA Nanopowder: Polythiophene- β -Naphtholsulphonic acid (PTh- β -NSA) Nanopowder was prepared by cationic surfactant assisted dilute polymerization method. In this method, thiophene monomer (0.1mol) was added drop by drop into 20 mL of chloroform containing 0.014 mol of surfactant (CTAB) and 0.4 mol of anhydrous FeCl₃ and 0.1 mol of β -Naphthol sulphonic acid under stirred condition. The ratio of [monomer] / [surfactant] was kept about 7/1¹⁴. The polymerization process was identified by changing the colour of

reaction mixture into brown. The polymerization was allowed to continuous stirring for 24 hour at 30°C. The dark-brown PTh- β -NSA nanopowder was collected by filtration of reaction mixture using distilled water with methanol until colourless filtrate was obtained. The PTh- β -NSA powder was dried under a vacuum oven at 80°C for 6 hour. The flowchart and reaction of PTh- β -NSA synthesis are shown in the figure-1.

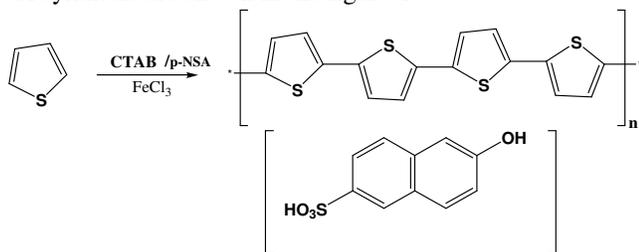


Figure-1
Synthesis of PTh- β -NSA nanopowder

The prepared PTh- β -NSA powder was confirmed by FTIR spectral studies and its particles size was measured by SEM studies and it was found to be in the range of 45-50 nm as shown in the figure-2.

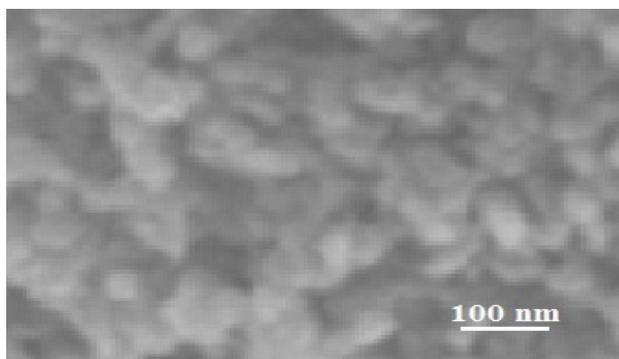


Figure-2
SEM image of PTh- β -NSA Nanopowder

Corrosion Inhibitor Studies: The weight loss and gasometric measurements were carried out as described elsewhere^{15,16}. Inhibition efficiencies for different concentrations of PTh- β -NSA were calculated in the absence and presence of the inhibitor at 30 in 1N HCl solution at 30°C.

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- β -NSA at 30°C. From the initial and final weight of the specimen, the loss in weight was calculated at various immersion time. The degree of surface coverage (θ) was calculated from the weight loss measurements and the data were tested graphically for fitting a suitable isotherm.

The potentiodynamic polarization measurements were carried out using EG and G PAR potentiostat /galvanostat (model -173)

analyzer a universal programmer in a conventional three-electrode glass cell at a sweep rate of 1mV per second. Both anodic and cathodic polarization curves were recorded in the absence and presence of an optimum concentration of PTh- β -NSA from a cathodic to an anodic potential of ± 250 mV (vs SCE). From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated¹⁷.

The electrochemical AC-impedance measurements were performed using EG and G Electrochemical impedance analyzer (model – 6310) with M38 software as described earlier¹⁸. A plot of Z' vs Z'' were made. From the plots, the charge transfer resistance (R_t) were calculated and the double layer capacitance were also calculated¹⁸. The experiments were carried out in the absence and presence of an optimum concentration of PTh- β -NSA.

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- β -NSA in 1N HCl solution for an immersion period of 3 hours.

The hydrogen permeation study was carried out using an adaptation of the modified two compartment cell described earlier¹⁶. The permeation current was measured in 1N HCl medium in the absence and presence of an optimum concentration of PTh- β -NSA.

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 hours, the specimens were taken out, dried and kept in a dessicator. 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 were carried out with various concentrations of PTh- β -NSA ranging from 100-900 ppm to study the effect of concentration of the inhibitor and immersion time on the corrosion inhibition of PTh- β -NSA 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- β -NSA are listed in the table -1. It was found that with increase in concentration of the PTh- β -NSA from 100 to 700 ppm, the weight loss decreased and hence the inhibition efficiency increased from 75.4 % to 95.2%. Beyond this concentration (700 ppm) inhibition efficiency decreased from 95.2% to 92.7%. It confirms that the optimum concentration for maximum inhibition efficiency was found to be 700 ppm. The influence of various concentrations of the PTh- β -NSA on inhibition efficiency of carbon steel in 1N HCl as shown in the figure-3.

The effect of immersion time from 3 hours to 24 hours was also studied as shown in the table-2. The inhibition efficiency

decreased from 95.2% to 93.2%. The effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of an optimum concentration 700 ppm of PTh-β-NSA as shown in the figure-4. Though 93.2% inhibition efficiency was obtained even at 24 hours of immersion time, the maximum inhibition efficiency was found upto 6 hrs.

Table-1

Corrosion parameters obtained from weight loss measurements for carbon steel

in 1N HCl containing various concentrations of PTh-β-NSA

Conc. of PTh-β-NSA (ppm)	Weight Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	0.2860	118.16	-	-
100	0.0703	29.04	75.4	0.75
300	0.0506	20.90	82.3	0.82
500	0.0297	12.27	89.6	0.90
700	0.0137	5.66	95.2	0.95
900	0.0209	8.63	92.7	0.92

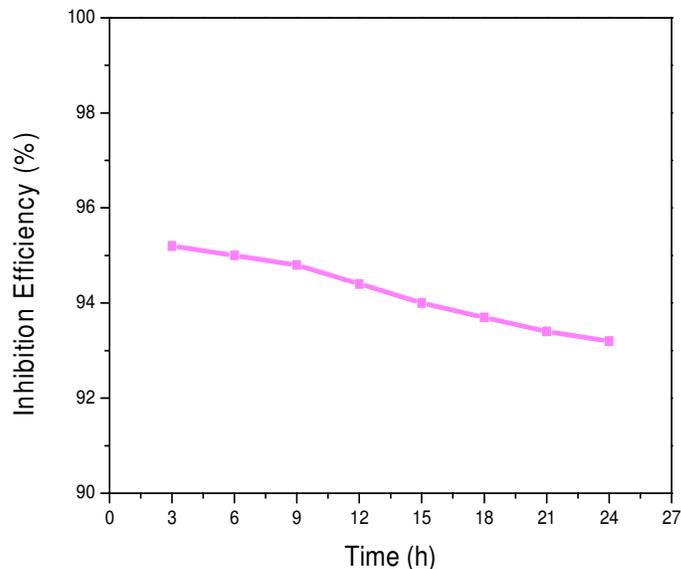


Figure-4

Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of an optimum concentration (700 ppm) of PTh-β-NSA

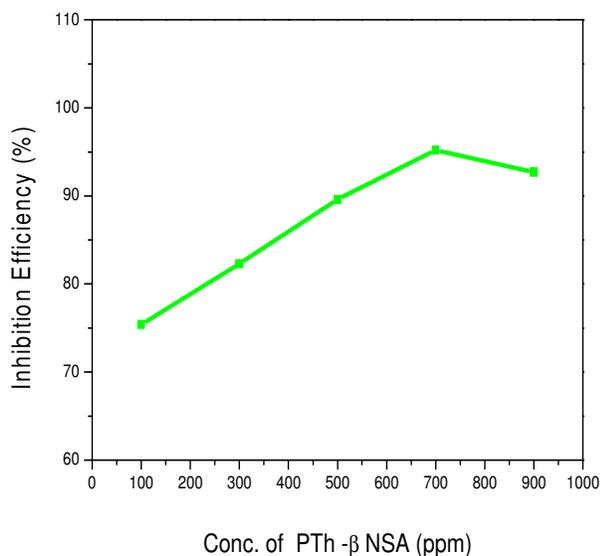


Figure-3

Variation of inhibition efficiency with concentrations of PTh-β-NSA on carbon steel in 1N HCl solution

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 concentration of PTh-β-NSA

System	Inhibition Efficiency (%)							
	Time (h)							
	3	6	9	12	15	18	21	24
700 ppm of PTh-β-NSA	95.2	95.0	94.8	94.4	94.0	93.7	93.4	93.2

Gasometric method: The table-3 shows the inhibition efficiency obtained from gasometric method for carbon steel in 1N HCl for various concentrations of PTh-β-NSA. It was observed that 7.2 mL of hydrogen gas was evolved with 1N HCl in the absence of the extract and with increase in concentration of PTh-β-NSA from 100 to 700 ppm, the volume of hydrogen gas evolved at 30± 1°C was found to decrease from 1.7 mL to 0.3 mL and at 900 ppm of PTh-β-NSA, the volume of hydrogen gas evolved increased from 0.3mL to 0.5mL. Hence the optimum concentration was found to be 700 ppm showing 95.8% inhibition efficiency. The volume of gas evolved for the corrosion of carbon steel in 1N HCl in the absence and presence of various concentrations of the PTh-β-NSA are presented in the figure- 5.

Table-3

Inhibition efficiency obtained from gasometric method for carbon steel in 1N HCl containing various concentration of PTh-β-NSA at 30°C

Conc. of PTh-β-NSA (ppm)	Volume of Hydrogen Gas Evolved (mL)	Inhibition Efficiency (%)
Blank	7.2	-
100	1.7	76.4
300	1.2	83.3
500	0.6	91.7
700	0.3	95.8
900	0.5	93.0

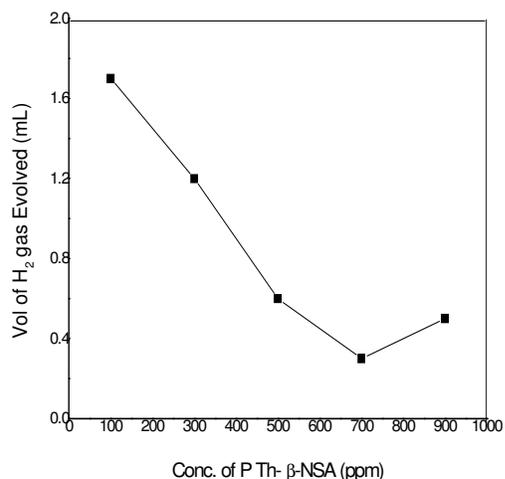


Figure-5

Variation of volume of gas evolved for the corrosion of carbon steel in 1N HCl of various concentration of PTh-β-NSA

Potentiodynamic Polarization Method: The polarization curves for carbon steel in 1N HCl with various concentrations of PTh-β-NSA as shown in the figure-6. It can be seen that the corrosion potential was not shifted significantly in presence of PTh-β-NSA control both anodic and cathodic reactions to inhibit the corrosion of carbon steel by blocking active sites on the carbon steel surface¹⁹. The potentiodynamic polarization parameters for carbon steel in 1N HCl in the absence and presence of an optimum concentration of PTh-β-NSA are given in the table-4. It can be seen that in the presence of an optimum concentration of inhibitor, the corrosion current decreased from 3.68 mA/cm² to 0.18 mA/cm². The extent of its decrease increased with PTh-β-NSA concentration from 100 to 700 ppm. This behaviour reflected the ability of PTh-β-NSA to inhibit the corrosion of carbon steel in 1N HCl. It was observed that with increase in concentration of PTh-β-NSA from 100 to 700 ppm, the maximum inhibition efficiency of 95.3% was observed.

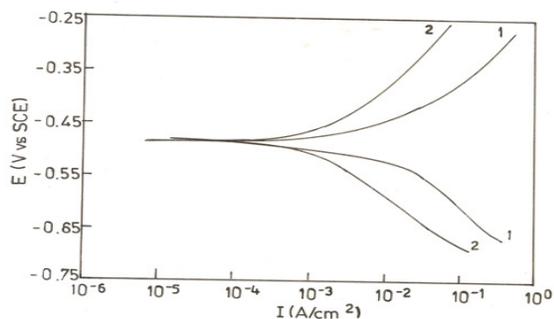


Figure-6

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

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

Conc. of PTh-β-NSA (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	-490	0.18	84.2	102.1	95.3

AC - impedance measurements: The corrosion behaviour of carbon steel in 1N HCl in the absence and presence of PTh-β-NSA was investigated by impedance method to find out the charge transfer resistance (R_t) and double layer capacitance (C_{dl}). From these parameters, the inhibition efficiency was calculated. The figure-7 shows the Nyquist plots for carbon steel in 1N HCl in the absence and presence of an optimum concentration of PTh-β-NSA and their corresponding impedance parameters are given in the table- 5. The obtained impedance diagrams were almost semi-circular in appearance due to the charge-transfer process that mainly controls the corrosion of carbon steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the homogeneity of the electrode surface arising from surface roughness or interfacial phenomena²⁰. The presence of PTh-β-NSA enhanced the value of R_t in acid solution. The R_t value obtained in the absence of the inhibitor was 20.2 Ω cm² and it increased to 452Ω cm² on the addition of an optimum concentration of PTh-β-NSA from 700 ppm. The increase in the value of R_t with the inhibitor concentration has led to the increase in the corrosion inhibition efficiency. Similarly the double layer capacitance in the absence of PTh-β-NSA was found to be 5046μF/cm² and the value decreased to the maximum extent in the presence of PTh-β-NSA was 526μF/cm². The decrease in C_{dl} suggests that the adsorption of this inhibitor takes place on the metal surface in acid solution.

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

Conc. of PTh-β-NSA (ppm)	R _t (Ω cm ²)	C _{dl} (μF/cm ²)	Inhibition Efficiency (%)
Blank	20.2	5046	-
700	452	526	95.5

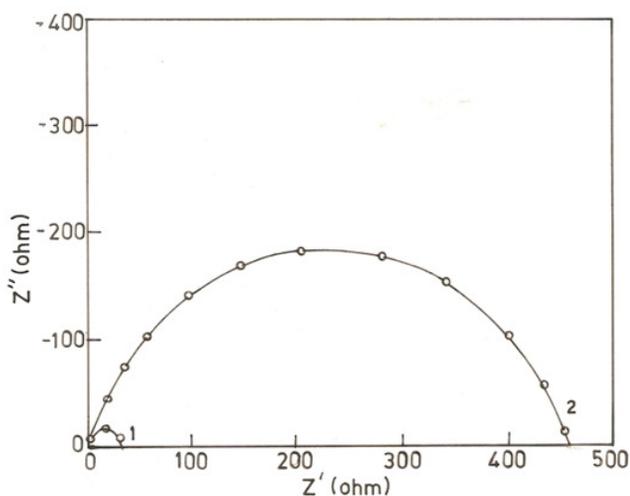


Figure-7

Impedance diagrams for carbon steel in 1N HCl solution in the absence and presence of an optimum concentration of PTh- β -NSA (1) Blank (2) 700 ppm of PTh- β -NSA

The maximum R_t value of $452\Omega\text{ cm}^2$ and minimum C_{dl} value of $526\ \mu\text{F}/\text{cm}^2$ were obtained at the optimum concentration 700 ppm of the PTh- β -NSA showed maximum inhibition efficiency of 95.5 %. A good agreement was observed between non-electrochemical and electrochemical polarization methods.

Effect of Temperatures: The effect of temperatures in the range 30°C to 90°C on the corrosion behaviour of carbon steel in 1N HCl in the absence and presence of the PTh- β -NSA was studied using weight loss method as shown in the table-6 and figure-8. 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. The PTh- β -NSA would have adsorbed on the carbon steel surface at all temperatures studied. As temperature increased from 30°C to 90°C, the inhibition efficiency was found to be decreased from 95.2 % to 88.2 %. This suggests that the adsorption of the PTh- β -NSA on the carbon steel may be due to physisorption.

Table -6

Corrosion of carbon steel in 1N HCl at different temperatures obtained by weight loss method in the absence and presence of an optimum concentration of 700 ppm of PTh- β -NSA

System	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	118.16	-
	50	147.91	-
	70	186.21	-
	90	239.90	-

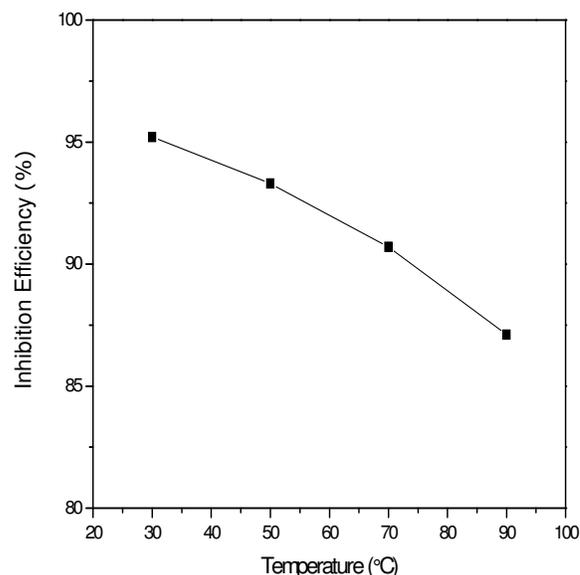


Figure-8

Effect of temperature on the corrosion inhibition efficiency of carbon steel in 1N HCl in presence of an optimum concentration(700ppm) of PTh- β -NSA

Mechanism for the corrosion inhibition of PTh- β -NSA: The Arrhenius plot for carbon steel immersed in 1N HCl solution in the absence and presence of an optimum concentration (700 ppm) of PTh- β -NSA as given in the figure-9. 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 the table-7. The activation energy (E_a) was found to be 10.95 KJ mol^{-1} for 1N HCl and increased to 26.14 KJ mol^{-1} in the presence of PTh- β -NSA, suggesting that the adsorbed organic matter formed a physical barrier to charge and mass transfers, leading to reduction in corrosion rate. The higher value of E_a in presence of the inhibitor compared to that in the absence of the inhibitor was attributed to physisorption^{21,22}.

The negative sign of free energy of adsorption indicates that the adsorption of PTh- β -NSA on carbon steel surface as a spontaneous process. The ΔG° values are in the range $-18.54\text{ KJ mol}^{-1}$ to $-18.96\text{ KJ mol}^{-1}$.

As the values of free energy of adsorption are less than -20 KJ mol^{-1} , the mode of adsorption is physisorption. The positive values of enthalpy of adsorption (ΔH) shows that the reaction is endothermic and the adsorption of the inhibitor on the metal surface took place. Entropy of adsorption (ΔS) remained a positive value and this reflects the formation of an ordered stable layer of the inhibitor molecule on the surface. The positive value of entropy indicates that the reaction was spontaneous and feasible.

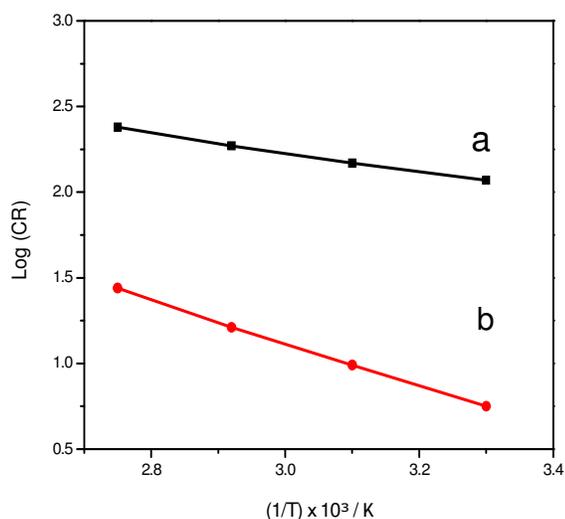


Figure-9

Arrhenius plots for carbon steel immersed in 1N HCl solution in the absence and presence of an optimum concentration of PTh-β-NSA (a) Blank (b) 700 ppm of PTh-β-NSA

Table-7

Calculated values of activation energy (E_a), enthalpy of adsorption (ΔH), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS) for carbon steel in the absence and presence of an optimum concentration 700 ppm of PTh-β-NSA in 1N HCl solution

System	Temp. (K)	E_a (KJ mol ⁻¹)	ΔG° (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	ΔS (KJ mol ⁻¹)
Blank	303	-	-	8.43	-
	323	9.14	-	8.26	-
	343	10.61	-	8.10	-
	363	13.11	-	7.93	-
700 ppm of PTh-β-NSA	303	-	-18.54	23.62	0.1391
	323	23.0	-18.82	23.45	0.1309
	343	25.31	-18.94	23.29	0.1232
	363	30.12	-18.96	23.12	0.1159

The polymeric inhibitor, PTh-β-NSA could adsorb on the metal surface via the lone pair of electrons present on their nitrogen atoms. The inhibitor might have adsorbed on the surface of the carbon steel and formed a compact protective thin layer on the surface of carbon steel. The corrosion of carbon steel in HCl solution is heterogenous one, composed of anodic and cathodic reactions. The adsorption of PTh-β-NSA molecules on the carbon steel surface makes a barrier for mass and charge transfers. This situation leads to a protection of carbon steel surface from the attack of the aggressive ions of acid solution. The degree of protection increased with increasing of the surface fraction occupied by the adsorbed molecules. As the inhibitor concentration increased, the number of adsorbed molecules on the surface increases.

The surface coverage (θ) was calculated from the inhibition efficiency values using weight loss method, and used to represent the fraction of the surface occupied by the adsorbed molecules. The values of surface coverage (θ) for various concentrations of the inhibitor are given in the table-1. The use of adsorption isotherms provided useful insight into the corrosion inhibition mechanism. A plot of C/θ versus C gave a straight line with unit slope suggests that the adsorption of various concentrations of PTh-β-NSA on the surface of carbon steel in 1N HCl followed Langmuir adsorption isotherm are presented in the figure-10.

Surface Analysis: The carbon steel specimens, after immersion in 1N HCl solution for 3 hours at 30°C in the absence and presence of an optimum concentration 700 ppm of the PTh-β-NSA, were taken out, dried and kept in a dessicator. Surface examination revealed the presence of a film as shown in the figure-11a & b.

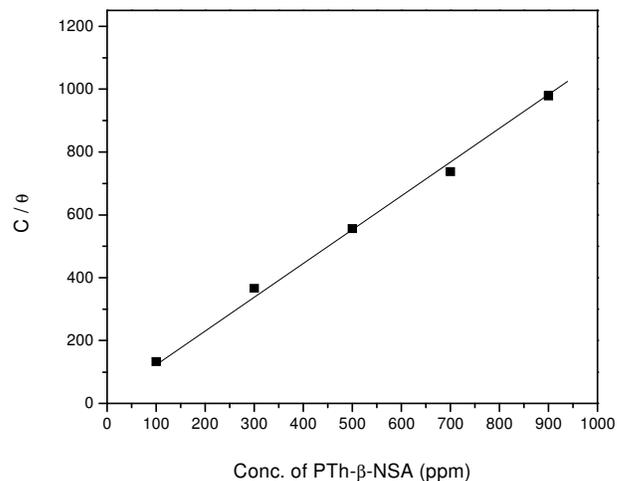


Figure-10

Langmuir adsorption isotherm plot for the adsorption of various concentration of PTh-β-NSA on the surface of carbon steel in 1N HCl solution

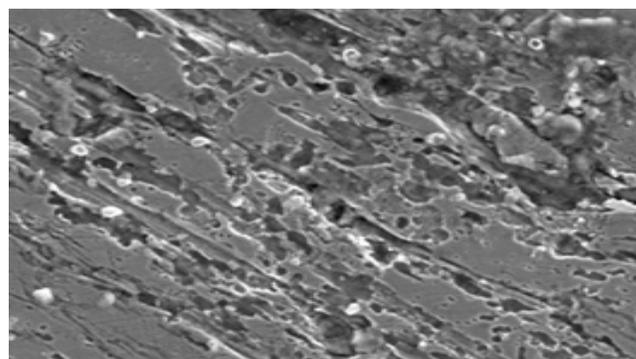


Figure-11a

SEM Photograph of carbon steel immersed in 1N HCl solution (blank)

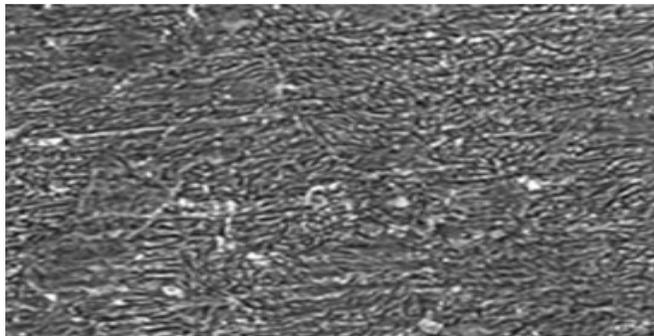
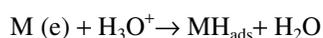


Figure-11b

SEM Photograph of carbon steel immersed in 1N HCl solution containing an optimum concentration (700 ppm) of PTh-β-NSA

Hydrogen Permeation Studies: The hydrogen permeation currents were recorded both in the absence and presence of PTh-β-NSA. This study has been taken up with an idea of confirming the inhibitor effectiveness on the reduction of hydrogen uptake. There are basically two reaction schemes²³. The first step is the diffusion of few hydrogen atoms that gets on to the electrode surface. Hydrated protons are reduced to form neutral hydrogen atoms upon those areas of the surface, which are unoccupied. One can say protons are discharged on to free sites on the electrode to form adsorbed hydrogen atoms.

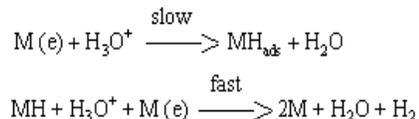


Where, M is the cathodic metal surface.

The second step is the desorption step and its two basic reaction paths are: i. Discharge D, followed by chemical desorption, CD. $MH_{ads} + MH_{ads} \rightarrow 2M + H_2 \uparrow$, ii. Discharge D, followed by electrolytic desorption, ED $MH_{ads} + H_3O^+ + M(e) \rightarrow 2M + H_2O + H_2 \uparrow$

For transition metals, it has been reported that the electrolytic desorption is the rate determining step. A part of the atomic hydrogen liberated during these processes enters the metal, when the remainder is evolved as hydrogen gas.

The permeation current vs time curves for carbon steel in 1N HCl in the absence and presence of PTh-β-NSA are shown in the figure-12 and their corresponding reduction in permeation current is given in the table-8. It shows that the prepared PTh-β-NSA was able to reduce the permeation current (84.3 %) compared to the control, which is almost same, as inhibition efficiency obtained from weight loss measurements. A definite correlation exists between the extent of corrosion inhibition and the percentage decrease in permeation current. The reason for the reduced permeation currents in presence of PTh-β-NSA can be attributed to the slow discharge step followed by fast electrolytic desorption step.



This sequence leads to lesser surface concentration of the adsorbed hydrogen atoms and the consequent reduction in the permeation current.

Table-8

Values of hydrogen permeation current for the corrosion of carbon steel in 1N HCl alone and in the presence of an optimum concentration of inhibitors

Inhibitor	Conc. Of Inhibitor (ppm)	Permeation Current (μA)	Reduction in Permeation Current (%)
Blank	-	23.6	-
PTh-β-NSA	700	3.7	84.3

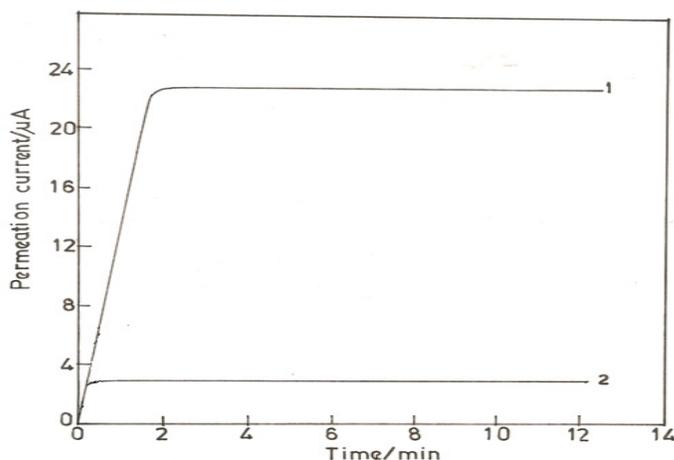


Figure-12

Hydrogen permeation current vs time plots for carbon steel in 1N HCl in the absence and presence of an optimum concentration of inhibitors (1) Blank (2) PTh-β-NSA (700 ppm)

Conclusion

PTh-β-NSA performs well in 1N HCl solution and inhibits the corrosion of carbon steel in 1N HCl solution at a concentration of 700 ppm. PTh-β-NSA controls both anodic and cathodic reactions by blocking the active sites of steel surface and it is the inhibitor of mixed type. The adsorption of PTh-β-NSA on carbon steel surface in 1N HCl solution is found to obey Langmuir adsorption isotherm. PTh-β-NSA is able to decrease the hydrogen permeation current effectively upto 84.3% in 1N HCl solution. The SEM analysis confirmed the protective nature of the metal surface by PTh-β-NSA.

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