Research Paper   Open Access

Inhibitive Effect of Hydrofluoric Acid Doped Poly Aniline (HF-PANI) on Corrosion of Iron in 1N Phosphoric Acid Solution

G.Maheswari*[1], P.Madhu [2], M.Sivaraju[3]

[1,2,]*Department of Chemistry, Thiruvalluvar govt arts college, Rasipuram, Tamilnadu, India.*
[3]*Department of Chemistry ,Muthayammal Technical Campus, Rasipuram, Tamilnadu, India*
.

Abstract- *The inhibition effect of Hydrofluoric acid doped poly aniline HF-PANI on mild steel corrosion in 1N phosphoric acid has been studied by mass loss and polarization techniques and AC impedance measurements methods between 303 K and 333K.The inhibition efficiency increased with increase in concentration of HF PANI. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. Potentiostatic polarization results revealed that HF-PANI act as mixed type inhibitor. The inhibitor of HF-PANI was chemically adsorbed and spontaneous adsorption on the mild steel surface .The values of activation energy (Ea), free energy of adsorption (ΔG_{ads}), heat of adsorption (Q_{ads}), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated. The adsorption of inhibitor on mild steel surface has been found to obey Temkin's adsorption isotherm. SEM analysis was agreed to establish the mechanism of corrosion inhibitor on mild steel corrosion in phosphoric acid medium.*

Keywords: *Corrosion inhibition; AC impedance measurements; Potentiostatic polarization; HF-PANI*

I.   INTRODUCTION

        Corrosion inhibitors are generally used in industry to reduce the corrosion rate of metals and alloys in making contact with unhelpful environment. Acids are widely used in industry such as pickling cleaning decaling ect. Because of their aggressiveness inhibitors are applied to reduce the rate of unexpected metal dissolution .[1-3]organic compounds rich in hetero atoms such as nitrogen ,oxygen ,unsaturated bonds and the plane conjugated system have been reported as effective inhibitors. In the past few years conducting polymers have been recognized as excellent corrosion inhibitor for the metals. A small quantity of polymer may be effective in inhibiting the corrosion of metals in acidic medium polyaniline has been high environmental stability ,how ever the highly insoluble nature of PANI in aqueous medium is the major limitation in corrosion inhibition application .[4-6]

        So, in this present investigation, the corrosion of mild steel in 1N phosphoric acid solution in the absence and presence of HF-PANI at 303 to 333K has been studied by mass loss and polarization methods. It is aimed to calculate the corrosion rate, inhibition efficiency on mild steel corrosion and the thermodynamic feasibility of inhibition via surface coverage on mild steel by adsorbed HF-PANI at various temperatures. The adsorption characteristic of HF-PANI was studied in order to access the mechanism of corrosion inhibition and the adsorption isotherm (s).

II.   EXPERIMENTAL DETAILS

2.1. Sample Preparation

Rectangular samples of area 5 cm x1 cm have been cut from a large sheet of mild steel. The samples were polished , drilled a hole at one end and numbered by punching .The surface of specimens was polished with emery papers ranging from 110 to 410 grade sand decreased with trichloroethylene specimens were dried and stored in desiccators for further use.
                      Table 1Composition of mild steel**:**

2.2. Preparation of Hydrofluoric acid doped Polyaniline:

        0.1 mol of aniline was dissolved in 0.1L of 1 mol L^{-1} HCl solution, 0.1 mol ammonium per sulphate solution as oxidant was slowly added with constant stirring for about 1 h. After the addition, the stirring continued for 6 h to ensure complete polymerization. The dark green colored polymer powders were filtered and washed with distilled water. The obtained powders were doped by stirring in 0.1 mol of aqueous ammonia

solution for 4 h. After the doping procedure, PANI powders were filtered and washed repeatedly with distilled water and dried in a vacuum oven at45ᵒC for 48 h.

Some of the synthesized powders were dispersed in 0.2 L of 2 mol L^{-1} solution of hydrofluoric acid. The mixture was constant stirred for about 0.5 h at ambient temperature, the precipitate were filtered after 24 h and dried in a vacuum oven at 45C for48 h to yield hydrofluoric acid doped PANI

From the residue the various concentrations of inhibitor solutions (1 to 5 mg) were prepared. Experiments were carried out in the presence and in the absence of HF-PANI in 1N Phosphoric acid

2.3. Characterization of HF Pani
It shows the FT-IR absorption spectroscopy of the two kinds of the synthesized powders. For the FT-IR spectroscopy of the synthesized emeraldine base PANI, the vibration at 1584 cm⁻1 is for the quinoid ring, while the vibration at 1493 cm⁻1 depicts the presence of benzenoid ring unit Furthermore, the peak at 1299 cm^{-1} is related to the C–N stretching of a secondary aromatic amine. The peak at 1160 cm⁻1 is assigned to vibrations associated with the C–H of N=Q=N (Q = quinoid ring). These results suggest that the synthesized powder was PANI in emeraldine state. Contrary to the FT-IR absorption spectra of emeraldine base PANI, the positions of several peaks of hydrofluoric acid doped PANI shifted towards lower wave numbers. For instance, the absorption peaks of the quinoid ring structures moved from 1584 and 1160 cm^{-1} to 1560 and 1112 cm^{-1}, respectively. The peak for benzene ring at 1493 cm⁻1 shifted to 1483 cm⁻1. Therefore, hydrofluoric acid do pants mainly located around nitrogen atoms in the quinoid ring rather than in the benzenoid ring. The FT-IR results showed that hydrofluoric acid had doped onto the PANI.

Figure 1 **FT**-IR spectrum of HF PANI

2.4. Weight loss measurement:
Polished specimens were initially weighed in an electronic balance. Behind that the specimens were balanced with the help of PTFE threads and glass rod in 100ml beaker containing acid in the presence and absence of HF-PANI. The specimens were removed after 4 hours washed with water to eliminate any corrosion products and finally washed with acetone. After that they were dried and reweighed. Weight loss method was carried out in 1N phosphoric acid with HF-PANI in the concentration range of 1mgs to 5 mgs as inhibitors and the temperature between 303 K and 333 K for an immersion period of 4 hours. Mass loss measurements were performed as per ASTM method described previously.

2.5. Potentio static polarization
Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer except for an exposed area of 1 cm^{2} were used as the working electrode. The saturated calomel electrode and the platinum foil were used as reference and counter electrodes respectively. The potentiostatic polarization measurement was carried out using BAS – 100, a model instrument. The potential of the test electrode was measured with respect to SCE, platinum electrode was used as auxiliary electrode and the experiment was carried out at 303K to333K.

$$IE\ (\%) = \frac{Icorr - I*corr}{ICorr} \times 100$$ ----------------- [1]

Where Icorr and I*corr are corrosion current in the absence and presence of an inhibitor.
.
2.6. SEM Analysis
The mild steel specimens were exposed in 100 ml of 1N Phosphoric acid solution having 5 mgs of plant extract for 3 hours at room temperature and washed with distilled water then dried. The nature of film formed on the surface of the metal specimens was analyzed by FT-IR and SEM. The dried specimens were scratched off and the resultant powder mixed with KBr (1:100 ratio) to prepare pellets, then the pellets was introduced into Fourier Transfer Infra-Red spectrophotometer FT-IR, 8400's SHIMADZU, Japan to analyze the sample.

III .RESULT AND DISCUSSION

3.1. Weight loss method
For weight loss experiments, mild steel specimens were immersed in 1N H₃PO₄ solution (100ml) for an optimized time period (3hours). An effect observed and analyzed by comparing the data obtained without and with different concentration of HF -PANI.
Corrosion rate (CR) is directly proportional to the weight Loss Cm^{-2} in a specified time and was calculated (mmpy) by the formula.

$$CR = \frac{87.6 \times W}{\rho \times A \times T} \qquad \text{--------------- [2]}$$

Where, W = weight loss in mg, ρ = density (7.51 g/cm3 for mild steel) of material used, A = area in cm^2 and t = exposure time in hours.

Table-1 show the value of inhibition efficiency (IE %), surface coverage (θ) and corrosion rate obtained at different concentration of the inhibitors in 1N phosphoric acid solution for an immersion period of 3 hours. From the mass loss value, the inhibition efficiency (IE %), surface coverage (θ) was calculated using the following equation.

$$IE\ (\%) = \frac{Wu - Wi}{Wu} \times 100 \qquad \text{------------- [3]}$$

$$\Theta = \frac{Wu - Wi}{Wu} \qquad \text{----------------- [4]}$$

Where Wu and Wi are the corrosion rates of mild steel in the absence and presence of inhibitor respectively at the same temperature .The inhibition efficiency increased with increase in concentration of inhibitors and decreased the temperature from 303K to 333K in 1N phosphoric acids shown in Table-2.

Table-2 Corrosion performance of mild steel in 1N phosphoric acid with HF -PANI at various temperatures (303K -333K

Figure 2 Corrosion behavior of mild steel in 1N phosphoric acid with HF -PANI at various temperatures (303K -333K)

3.2. Potentiostatic polarization curves

The Polarization behavior of mild steel functioning as cathode as well as anode in the test solution is shown in fig.3 for 1N phosphoric acid with HF-PANI at room temperature (303K). The electrochemical data obtained are shown in Table I. It is evident that HF-PANI brings about considerable polarization of cathode as well as anode. HF-PANI acts as a mixed type inhibitor. The non-constancy of Tafel slopes for different inhibitor concentration revealed that the inhibitor act through their interference in the mechanism of the corrosion processes at the cathode as well as anode. The i_{corr} values were decreased with increasing concentration of the inhibitors which indicate that the corrosion process is controlled by adding HF-PANI.

Figure 3 Potentio dynamic polarization for mild steel in 1N H$_3$PO$_4$ containing various concentration of HF-PANI.

3.3. A.C Impedance Measurements

A.C impedance measurements were carried out for corrosion of mild steel in 1N phosphoric acid after immersion for about 20 minutes at room temperature (303K). The impedance diagrams for mild steel in 1N phosphoric acid for the various concentrations of the HF-PANI are shown in Figures 2.

The impedance parameters and the inhibition efficiency of HF-PANI for mild steel in 1N phosphoric acid are given in Table 2. The values of charge transfer resistance (R_{ct}) for mild steel in phosphoric acid significantly changed after the addition of HF-PANI. The inhibitor efficiency and R_{ct} values increased with increase in concentration of HF-PANI. The semicircular nature of Nyquist plots obtained for all the experiments indicated that the corrosion of mild steel is controlled purely by charge transfer process. Higher R_{ct} values in the case of 1N H$_3$PO$_4$ with HF-PANI indicate that the strongly adsorbed on the surface of mild steel. The double layer capacitance (C_{dl}) decreased with increase in concentration of HF-PANI. The decrease in C_{dl} values in the presence of HF-PANI indicated the fact that these additives inhibit the corrosion by adsorption on the metal surface. The inhibition efficiency obtained from A.C impedance measurements are in good agreement with those obtained from weight loss and potentiostatic polarization studies. [6]

Table 2 A.C impedance parameters of mild steel in 1N Phosphoric acid in the presence and absence of HF-PANI at 303K

Figure 4 A.C impedance parameters of mild steel in 1N Phosphoric acid in the presence and absence of HF-PANI at 303K

3.4. Thermodynamic parameters:

Theoretical fitting of the corrosion data to the kinetic thermodynamic model was tested to show the nature of adsorption. Table 4 shows that the calculated values of energy of activation (Ea) for mild steel corrosion in 1N phosphoric acid with and without inhibitor from 303K to 333K. Energy of activation (Ea) was calculated from Arrhenius equation. [7]

$$Log(\frac{P2}{P1}) = Ea/2.303R[\frac{1}{T1} - \frac{1}{T2}] \qquad \text{------------------- [6]}$$

Where P1 and P2 are corrosion rates of mild steel at the temperatures T$_1$ (303K) and T$_2$ (313K) respectively. The values of heat of adsorption (Q $_{(ads)}$) were calculated using the following equation.

Q (ads) = 2.303Rlog$[\frac{\theta2}{1-\theta2} - \frac{\theta1}{1-\theta1}] \times \frac{T1 \times T2}{T2-T1}$ -------------- [7]

Where θ_1 and θ_2 are surface coverage of the inhibitor at the temperatures T_1 (303K) and T_2 (313K) by the different additives.

The free energy of adsorption [$\Delta G_{(ads)}$] was calculated from the following equation

$\Delta G_{(ads)}$ = -RT ln (55.5K)   -------------- [8]

and K is given by

K= θ /C (1- θ)   ----------------------------- [9]

Where θ is surface coverage on the metal surface, C is the concentration inhibitor in mole/lit and K is the equilibrium constant. [8]

The enthalpy of adsorption (ΔH) was calculated using the equation

$\Delta H = Ea - RT$ ------------------------ [10]

The entropy of adsorption (ΔS) was calculated using the equation

$\Delta G = \Delta H - T\Delta S$ ---------------------- [11]

The calculated values of energy of activation (Ea), heat of adsorption Q $_{(abs)}$, free energy of adsorption [ΔG (ads)], enthalpy of adsorption (ΔH), the entropy of adsorption (ΔS) are shown in Table 3.

In this case the negative sign of free energy of adsorption (-ΔG(ads)) for HF-PANI indicates that the adsorption of the mild steel surface was a spontaneous process band the adsorption could be chemisorptions. The negative value of enthalpy of adsorption (ΔH) indicates that the reaction was exothermic and adsorption of the inhibitor on the metal surface has taken place.[9-10]

Table-3 Thermodynamic parameter for mild steel in 1N H_3PO_4 with HF-PANI at various temperatures (303K - 333K)

3.5. Adsorption isotherms.

The adsorption of HF-PANI on the metal surface and the interaction between the organic compounds and metal surface, various adsorption isotherms have been tested with several adsorption isotherms such as Langmuir adsorption isotherm known as thermodynamic /kinetic model and Florry- Hyggins model was found to be closest to description of adsorption behavior of the inhibitor, [9-11]under investigation. The plot of θ versus log$C$ give a straight lines of slope(X) and intercept (K') for Temkin adsorption isotherm with HF-PANI as shown in Figures 8

The plot of log[$\theta/(1-\theta)$] versus log$C$ give a straight lines of slope(X) and intercept (K') for kinetic model for HF-PANI (El-Awady et al) as shown in Figures 6. The values of equilibrium constant K (K=k'.1/y), change in the free energy of adsorption (ΔG_{ads}) and number of inhibitor molecules occupying one active site (x) are present in Table 4. Inspection of this table shows that the numbers of active sites are nearly constant and approximately equal to one at all temperatures. [12-13]

This behavior can be discussed on the basis that the adsorption process takes place by the occupation of one active site by a single inhibitor molecule. Also, the equilibrium constant K' decreases with increasing the temperature suggesting that this inhibitor is strongly adsorbed on metal surface at room temperature but desorption process enhanced at higher temperature. Large values of K' mean better inhibition efficiency of a given inhibitor, strong electric interaction between the double layer existing at the phase boundary and the adsorbing molecules. Small values of K', however compromise that such interactions by adsorbing molecules and the metal surface are weaker, denoting that the molecules are easily removable by the solvent molecules from the surface. The negative values of standard free energy of adsorption (ΔG_{ads}) are large and indicate that the adsorption reaction was spontaneous.

According to Flory–Huggins isotherm, a plot of log θ/C versus log [$1-\theta$] gave straight lines of slope (x) intercepts (log XK) and regression coefficients (R2) of HF-PANI are shown in Figures 5. Table 4 gives curve fitting data to Flory–Huggins isotherm. It is seen that, there is a good agreement between the values of K', 1/Y, X, K and ΔG_{ads} obtained from the kinetic model and Flory–Huggins isotherms. The numerical values of K obtained from the Langmuir thermodynamic/kinetic model and Flory–Huggins isotherm are found to be 3123 and 3060 for HF-PANI respectively at 303K. They showed as the temperature increases, the K value decreases when compared with 303K. The higher values of K and $\Delta G°_{ads}$(-30.73 kJ/mole) indicate that the HF-PANI strongly adsorbed on mild steel leads to the inhibition efficiency of HF-PANI (97.36%) and found to be higher. The regression coefficient (R^2) values obtained from kinetic model for HF-PANI are higher when compared with the values obtained from Flory–Huggins isotherm. It indicates that the kinetic model was fit for adsorption of HF-PANI on mild steel.[14-16]

Table 5.Adsorption isotherm parameters of HF-PANI for mild steel in 1N H_3PO_4 by Kinetic model and Florry-Hyggins Model

Figure: .5. Arrhenius plot of HF-PANI for mild steel corrosion in 1N Phosphoric acid

Figure 6 Langmuir adsorption isotherm plot of HF-PANI for mild steel in 1N H_3PO_4

Figure 7. Flory–Huggins adsorption isotherm plot of HF-PANI for mild steel in 1N H_3PO_4
Figure 8. Temkin adsorption isotherm plot of H-PANI for mild steel in 1N H_3PO_4

3.6. SEM analysis

Scanning Electron Microscope images were taken in order to study the changes that occur during the corrosion of mild steel in the presence and absence of the green inhibitor Fig -(9-10) represents the micro graphs of the mild steel samples after exposure to the corrosive environments. Although they show different morphologies, both portrayed severely damaged surface due to the formation of corrosion products. No pits and cracks are observed in the micro graphs after impression of inhibitors in the corrosive media Fig-(10) expect polishing lines, The metal surface was homogeneously covered with the inhibitor molecules .Consequently forming a protective film.
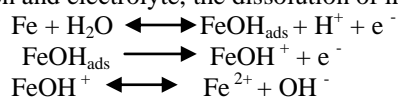
Figure 9. SEM analysis of Mild steel in 1N Phosphoric acid
Figure 10. SEM analysis of Mild steel in 1N Phosphoric acid With HF PANI

3.7. Mechanism of corrosion inhibition

The composition and the structure of the films formed on iron remains subjects of continued interest from FTIR studies on the oxides of iron revealed the presence of Fe_2O_3 in solutions irrespective of the nature of the iron substrate.

At the interface of iron and electrolyte, the dissolution of iron can be written as,

$$Fe + H_2O \longleftrightarrow FeOH_{ads} + H^+ + e^-$$
$$FeOH_{ads} \longrightarrow FeOH^+ + e^-$$
$$FeOH^+ \longleftrightarrow Fe^{2+} + OH^-$$

At medium and high concentrations of phosphoric acid, precipitation of iron-phosphate occurs at interface.

$$6H_3PO_4 + 3Fe \longrightarrow 3\,Fe\,(H_2PO_4)_2 + 3H_2$$
$$3Fe\,(H_2PO_4)_2 \longrightarrow Fe_3\,(PO_4)_2 + 4H_3PO_4$$
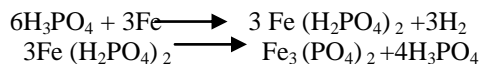
However, this precipitation can be weakly observed when the mild steel is treated with phosphoric acid solutions with low concentration. The formation of insoluble phosphate depends on the metal ions present in solutions at interface, concentration of metal ion in the solution and the reactivity of metal surface. G.Gunasekaran and L.R.Chauhan[8] explained that as soon as the HF PANI interacts with dissolving iron to form an organo-metel complex (Fe- HF PANI) and forms a layer.[17]

$$Fe^{2+} + HF\,PANI \longrightarrow [Fe\text{- HF PANI}]$$
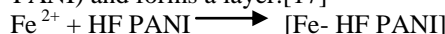
This layer reacts with phosphate ions to form a layer of $FeHPO_4/FeH_2PO_4$ to the formation of Fe- HF PANI, since it is mediated or catalyzed by this compound, as is observed by the increased rate of formation of iron phosphates. After certain period, the formation of iron phosphate results in a dense layer and formation of Fe- HF PANI will less. This was reflected by FT-IR analysis of mild steel immersed in 1N phosphoric acid containing 5mgs of HF PANI.

IV. CONCLUSION

1. Corrosion rates of mild steel in 1N phosphoric acid decreased with increasing concentration of HF-PANI.The inhibition efficiency increased with respect to the concentration of inhibitor and decreased with rise in temperature from 303K to 333K.
2. The maximum inhibition efficiency of HF-PANI was found to be 87.25 % and 81.92% in 1N phosphoric acid at 5mgs of inhibitor from mass loss studies and polarization measurement respectively at 303K.The inhibition efficiency obtained from mass loss and polarization measurement showed fairly good agreement.
3. Energy of activation (Ea) values indicated that the addition of HF-PANI hinders metal dissolution and also indicated that, decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature.
4. The negative value of ΔG_{ads} indicated that the HF-PANI was chemically adsorbed and spontaneous adsorption of inhibitors on the surface of mild steel.
5. The higher negative values of heat of adsorption also showed that the inhibition efficiency decreased with rise in temperature
6. The high positive enthalpy values of adsorption (ΔH_{ads}) evident that the plant extract strongly adsorbed on mild steel is probably chemisorptions.
7. The gain in entropy that accompanied by the substitution adsorption process was attributed to the increase in solvent entropy.
8. It is found that the HF-PANI acting as mixed type inhibitor.
9.   The adsorption of HF-PANI on mild steel surface from the acid solution followed Temkin's adsorption isotherm.
10. FT-IR and SEM analysis showed the presence of compounds in the plant extract react with metal ion to form the layer of inhibitor on the metal surface.

REFERENCE

[1]. Rajendran S, Sridevi SP, Anthony N, John Amalraj A, Sundearavadivelu M (2005) Corrosion behaviour of carbon steel in polyvinyl alcohol. Anti-Corros Method M 52(2):102–107

[2]. M.Atta Ayman, GamalA.El-Mahdy, AdelA.Azhary, HamadA.Al-Lohedan, (2013) Experimental Investigation and Theoretical Appproach on Water soluble Rosin as corrosion Inhibitor,Int.J.Electrochem .Sci.,8.,1295-1307

[3]. Solange .De souza,Smart coating based on polyaniline acrylic blend for corrosion protection of different metals,Surf.coat.Technol.,201.,7574(2007)

[4]. Abdel Rehim SS, Tohommy FM, Seleet MM (1984) Effect of some polyaminopolycarboxylic acids on the corrosion of steel in sulphate solutions. Surf Tech 21(2):169–1775.

[5]. Khairou KS, El Sayed A (2003) Inhibition effect of some polymers on the corrosion of Cd in a hydrochloric acid solutions. J Appl Polymer Sci 88(4):866–871

[6]. Manickavasagam R, Jeya K, Paramasivam M, Venkatakrishnalyer S (2002) Poly (styrene sulphonic acid) doped polyaniline as an inhibitor for the corrosion of mild steel in hydrochloric acid. Anti-Corros Method M 49(1):19–26

[7]. Quraishi. M.A and Khan. M. A. W, (2005) Thiadiazoles-A potential class of Heterocyclic inhibitor for Prevention of mild steel corrosion in hydrochloric acid solution Indian Journal of Chemical Tech., 12, 576-581 .

[8]. Umoren SA, Ebenso EE, Okafor PC, Ekpe UJ, Ogbobe O (2006) Effect of halides on the corrosion inhibition of mild steel in alkaline medium using polyvinyl alcohol. J Appl Polymer Sci 103:2810–2816

[9]. Gunasekaran. G and Chaughan. L.R, (2007).,Corrosion inhibition of mild steel by plant extract in dilute HCl mediumCorrosion Science., 49, 1143-1161.

[10]. Bentiss, M. Traisnel, L. Gengembre, and M. Lagrenée,(1999) "New triazole derivative as inhibitor of the acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS," Applied Surface Science, vol. 152, no. 3, pp. 237–249,

[11]. T. Szauer and A. Brandt,(1981) "On the role of fatty acid in adsorption and corrosion inhibition of iron by amine-fatty acid salts in acidic solution," Electrochimica Acta, vol. 26, no. 9, pp. 1219–1224,.

[12]. F. Bentiss, M. Lebrini, and M. Lagrenée, (2005)"Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4-thiadiazoles/ hydrochloric acid system," Corrosion Science, vol. 47, no. 12, pp. 2915–2931,

[13]. Weihua Li, Qiao He, Changling Pei, Baorong Hou , (2007) Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media,Electrochemica Acta., 52, 6386-6394

[14]. Oguzie, E. E. (2006) "Studies on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel," Materials Chemistry and Physics. 99(2-3): 441–446.

[15]. Chandrasekaran. V, Kannan. K and Natesan. M. Corrosion behaviour of mild steel in phosphoric acid medium with benzotriazole., (2004)., Journal of metallurgy and material Science., 46, 253

[16]. Putilova. I.N, Barannik. V and Balezin. S.S, (1960).The corrosion behavior of stainless steel in mixed anhydrous HNO$_3$ and. H$_2$SO$_4$ acid.,Metallic Corrosion Inhibitors, Pergamon Press, Oxford 30

[17]. Gunasekaran. G and Chaughan. L.R, Electrochemical Acta. (2004), Eco-Friendly Inhibitor for Corrosion Inhibition of Mild Steel in Phosphoric Acid.49, 4387-4395

Table 1Composition of mild steel:

Element	Fe	Ni	Mo	Cr	S	P	Si	Mn	C
Composition (%)	99.686	0.013	0.015	0.043	0.014	0.009	0.007	0.196	0.017

Table-2 Corrosion performance of mild steel in 1N phosphoric acid with HF -PANI at various temperatures (303K -333K

Temp (K)	Conc. of HF-PANI(mgs)	Mass loss studies			Polarization measurement					
		Corrosion Rate (mmpy)	Surface coverage (θ)	IE (%)	E_{corr} Vs SCE (mv)	I_{corr} $\mu A/cm^2$	Tafel constant mv/decade			IE (%)
							b_a	$-b_c$		
	Blank	159.25	-	-	-460	260	55	110		-
	1	48.79	0.6936	69.36	-465	54	41	110		79.23
	2	31.95	0.7994	79.94	-470	49	40	102		81.15
	3	22.38	0.8594	85.94	-470	45	42	98		82.69
	4	17.43	0.8905	89.05	-472	36	40	95		86.15
303	5	10.6	0.9334	93.34	-475	26	38	90		90
	Blank	182.73	-	-	-465	610	50	120		-
	1	60.48	0.669	66.9	-475	250	48	105		59.02
	2	50.03	0.7262	72.62	-470	200	42	100		67.21
	3	48.79	0.733	73.3	-480	162	44	98		73.44
	4	40.22	0.7799	77.99	-485	140	40	90		77.05
313	5	30.31	0.8341	83.41	-480	118	42	95		80.66
	Blank	217.06	-	-	-475	1050	65	135		-
	1	85.11	0.6075	60.75	-485	550	52	115		47.62
	2	78.16	0.6399	63.99	-475	460	50	105		56.19
	3	70.39	0.6757	67.57	-475	350	50	102		66.67
	4	64.44	0.7031	70.31	-470	270	45	95		74.29
323	5	38.88	0.8209	82.09	-477	255	40	92		75.71

	Blank	271.74	-	-	-480	1600	90	140	-
333	1	129.48	0.5235	52.35	-470	815	95	120	49.06
	2	120.12	0.558	55.8	-475	725	75	114	54.69
	3	114.62	0.5782	57.82	-480	615	60	102	61.56
	4	104.76	0.6145	61.45	-474	512	55	120	68
	5	99.56	0.6336	63.36	-482	475	60	100	70.31

HF-PANI (mg)	HF-PANI		
	R_{ct} (ohm cm^2)	C_{dl} (μF/cm^2)	IE (%)
Blank	152.78	6545.47	-
1	734.13	1362.14	59.72
2	919.63	1087.39	63.12
3	1087.14	919.84	68.16
4	1770.38	564.84	76.2
5	2773.9	360.5	81.17

Table-3 Thermodynamic parameter for mild steel in 1N H_3PO_4 with HF-PANI at various temperatures (303K -333K)

Conc. of inhibitor (mg)	E_a (from equ) kJ/mole	E_a (from plot) kJ/mole	-ΔG_{ads} kJ/mole				Q_{ads} kJ/mole	ΔH kJ/mole	ΔS kJ/mole
			303K	313K	323K	333K			
Blank	14.95	15.6	-	-	-	-	-	10.79	-
1	27.21	28.45	29.58	30.26	30.51	30.5	1.44	10.79	0.1773
2	36.92	25.14	29.26	29.16	29.02	28.97	4.49	23.05	0.2046
3	45.52	24.56	29.31	28.2	28.36	28.08	6.18	32.76	0.2309
4	49.99	26.15	29.31	28.11	27.93	27.7	9.98	41.36	0.2442
5	62.44	26.02	30.12	28.44	29.1	27.3	11.46	45.83	0.2893

Table 5.Adsorption isotherm parameters of HF-PANI for mild steel in 1N H_3PO_4 by Kinetic model and Florry- Hyggins Model

Inhibitor	Temp. (K)	Kinetic model				Florry- Hyggins Model			
		1/Y	K	-ΔG_{ads} kJ/mole	R^2	X	K	-ΔG_{ads} kJ/mole	R^2
TPWE	302	0.9349	3123	30.56	0.9611	0.8703	3060	30.34	0.9456
	313	2.0040	118	21.08	0.8510	1.899	1148	27.87	0.8950
	323	1.8041	111	21.86	0.9020	1.3133	333	24.75	0.9317
	333	3.5920	26	16.62	0.9542	2.1245	430	25.39	0.8870

Table 5.Adsorption isotherm parameters of HF-PANI for mild steel in 1N H_3PO_4 by Kinetic model and Florry- Hyggins Model

Inhibitor	Temp. (K)	Kinetic model				Florry- Hyggins Model			
		1/Y	K	-ΔG_{ads} kJ/mole	R^2	X	K	-ΔG_{ads} kJ/mole	R^2
TPWE	302	0.9349	3123	30.56	0.9611	0.8703	3060	30.34	0.9456
	313	2.0040	118	21.08	0.8510	1.899	1148	27.87	0.8950
	323	1.8041	111	21.86	0.9020	1.3133	333	24.75	0.9317
	333	3.5920	26	16.62	0.9542	2.1245	430	25.39	0.8870

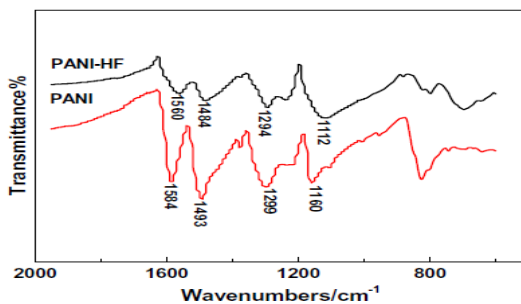Figure 1 **FT**-IR spectrum of HF PANI

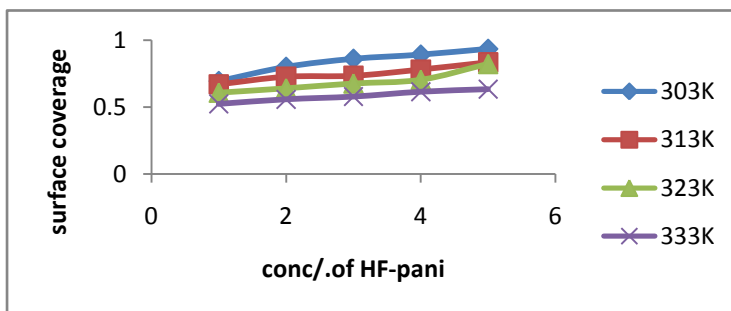Figure 2 Corrosion behavior of mild steel in 1N phosphoric acid with HF -PANI at various temperatures (303K -333K)

Figure 3 Potentio dynamic polarization for mild steel in 1N H_3PO_4 containing various concentration of HF-PANI.
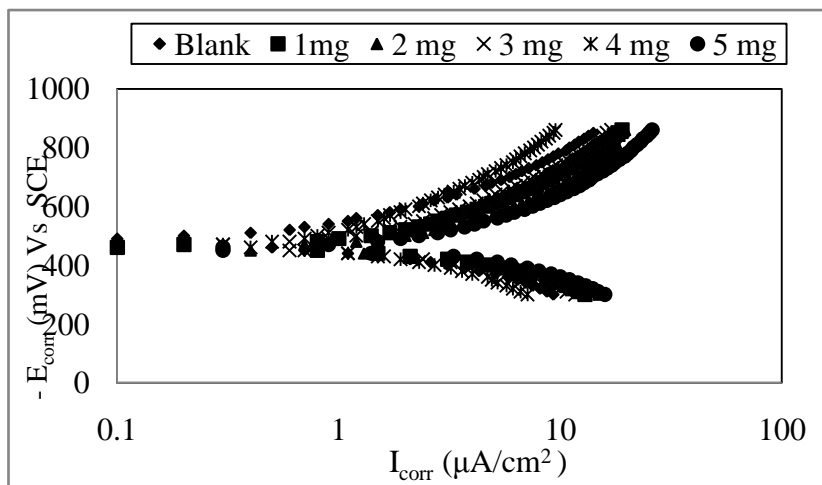

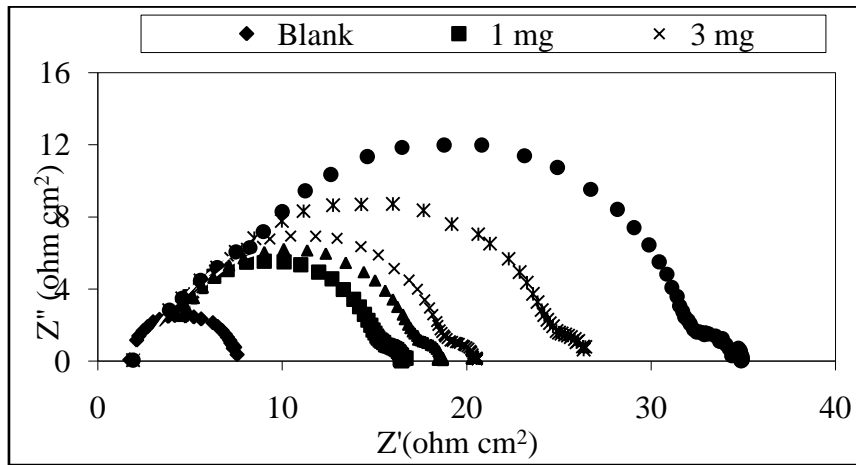Figure 4 A.C impedance parameters of mild steel in 1N Phosphoric acid in the presence and absence of HF-PANI at 303K

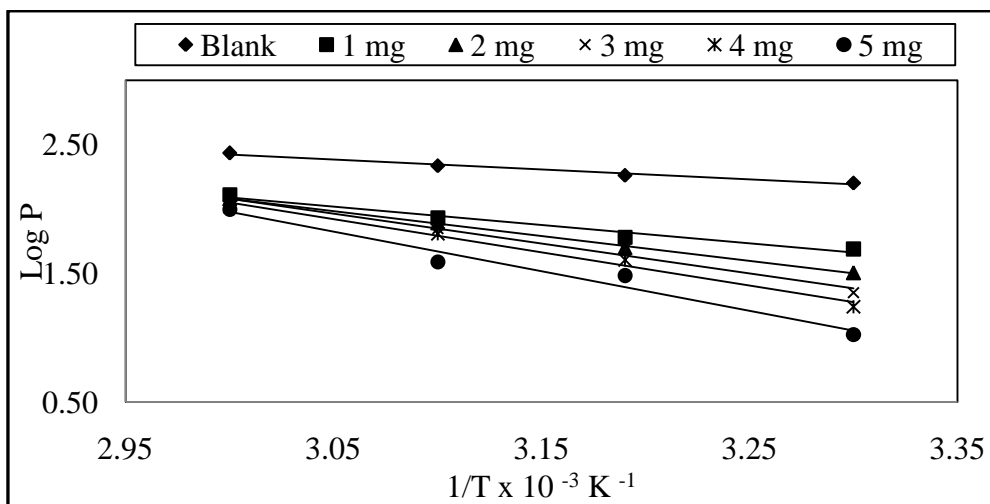Figure: .5. Arrhenius plot of HF-PANI for mild steel corrosion in 1N Phosphoric acid

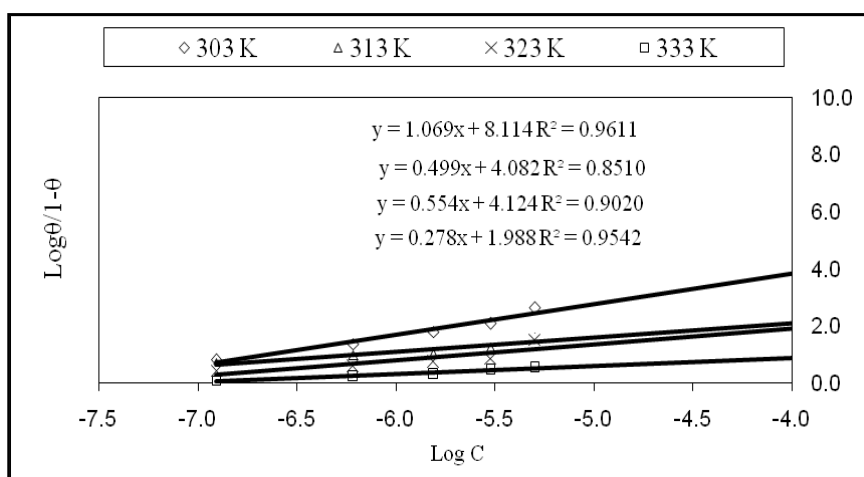Figure 6 Langmuir adsorption isotherm plot of HF-PANI for mild steel in 1N H_3PO_4

Figure 7. Flory–Huggins adsorption isotherm plot of HF-PANI for mild steel in 1N H_3PO_4
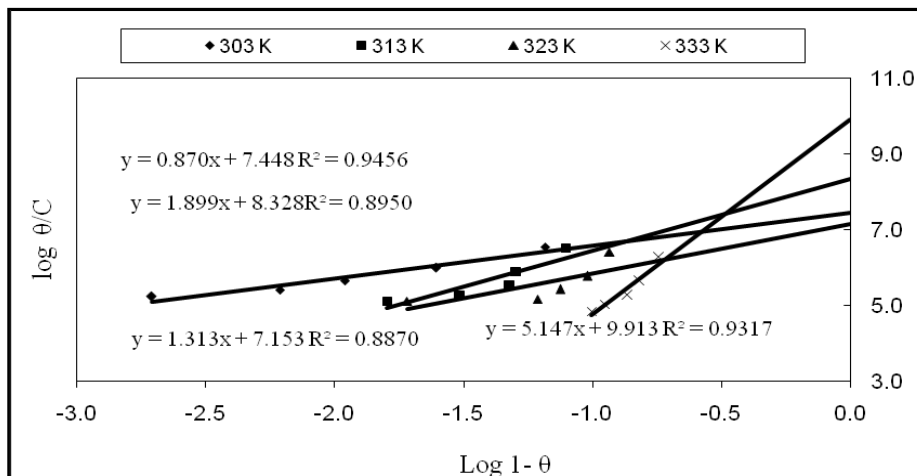
Figure 8. Temkin adsorption isotherm plot of HF-PANI for mild steel in 1N H_3PO_4
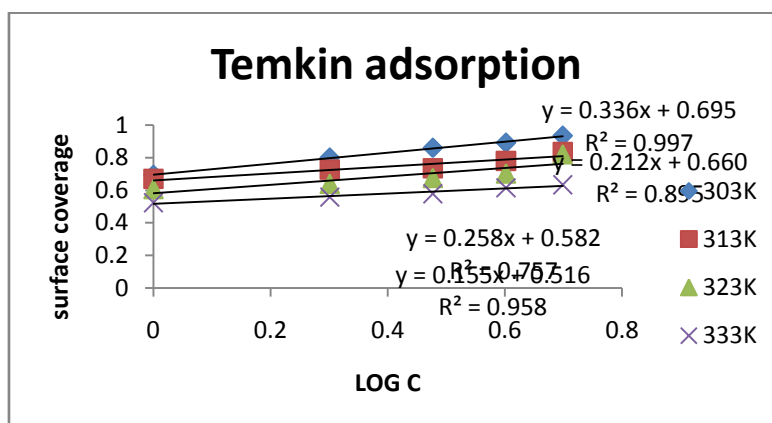

Figure 9. SEM analysis of Mild steel in 1N Phosphoric acid

Figure 10. SEM analysis of Mild steel in 1N Phosphoric acid With HF PANI