Research article

Corrosion Protection of Mild steel in Phosphate Fertilizer Industry by Organic inhibitors

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Abstract

Mild steel is a very important industrial metal and it uses in several operational units. Bulk amount of sulphuric acid is used with phosphate raw materials during production phosphate fertilizer. Mild steel is a sensitive metal in acidic medium. It startscorrosion reaction with metal. It changes their physical, chemical and mechanical properties, tarnishes their facial appearance and its deterioration occurs due to corrosion reaction. Metal is suffering from various types of corrosion like galvanic corrosion, pitting corrosion, crevice corrosion, stress corrosion and other types of corrosion.Organic inhibitors 2-(aminomethyl)phenol and 2-(aminomethyl)aniline are used as corrosion resistance for this work. These inhibitors anticorrosive properties studied at different temperatures 60^0C, 70^0C and 80^0C and 5mM theirconcentration. The corrosion rate of metal was calculated by gravimetric technique. Corrosion current density was determined potentiostatic polarization techniques. Inhibitors' surface adsorption phenomenon, thermal stability, physisorption-chemisorption activities, surface films formation were studied by application ofactivation energy, heat of adsorption, free energy, enthalpy and entropy. Inhibitors occupied space on interface i.e. confirmed by surface coverage area and inhibition efficiency. Potentiostat results were shown that these inhibitors developed polarization on the surface of base metal.**Copyright © WJIEMR, all right reserved.**

Keywords: Mild steel, inhibitors, gravimetric,potentiostat, polarization, thermal stability.

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Introduction

Corrosion is a major problem with materials. It cannot be fully controlled but its effect can be minimized with the help of suitable corrosion control techniques. It is major setback for economy because huge money expense for repairing, replacement and maintenance of equipments. Scientists and researchers used various techniquesfor corrosion protection for metals like designing proper shape and size of materials, metallic coating [Sekino T, etal. 2004], non metallic coating [Khram A N, etal.2004], organic and inorganic inhibitors, [Seth A, etal.2004] anodic and cathodic protection [Ianmuzzi M, etal. 2007], polymeric coating[Singh R K, etal. 2013], nanocoating[Singh R K, etal. 2013] and plasma coating [Singh R K etal.]. Metallic coating used for the corrosion mitigation of materials in H_2SO_4 environment.Polymeric coating applied in H_2SO_4 medium for the safety of metals but this acid produced disbanding between polymeric materials. Organic coatings [Moutarlier V, etal. 2008] provided protection of metal in corrosive environment but thesetypes of organic coatings were disbanded by sulphuric acid and it also created dissolving and swelling effect on their interfaces.Aliphatic and aromatic compounds [Code A, etal.2008] possessesing nitrogen, oxygen,sulphur and electron releasing functional groups were used as inhibitors in different hostile environment. Electrochemical technique [Shem M et al. 2009] like anodic and cathodic was applied for corrosion protection of metal but this technique didn't save metal for corrosion. The nanocating of inorganic and organic materials [Glezakou V A, etal.2009] exhibited anticorrosive results in these conditions. The nanocoating materials [Farias MCM, etal.2009] entered into the matrix of base metal and stopping formation of corrosion cell. Several types of nanocoating techniques [Cuevas-Arteaga C, 2008] were applied for corrosion control of metals like top barrier coating, thermal barrier coating, composite thin film coating and vapour deposition coating. For this work used inhibitors adhered with the base metal and formed surface films with metal.

Experimental

Mild steel coupons were cut into size of (10X5X0.01) cm^2. Its surface was rubbed with emery paper and samples were washed with double distilled water. Finally it was rinsed with acetone and dried with air dryer and kept into desiccator. The sample dipped 250ml biker and kept into thermostat to calculate corrosion rate at different temperatures. The corrosion rate was determined by gravimetric method without and with addition of inhibitors 2-(aminomethyl)phenol and 2-(aminomethyl)aniline.The corrosion current density and corrosion rate without and with inhibitors were calculated by potentiostatic polarization technique with help of an EG & G Princeton Applied Research Model 173 Potentiostat. A platinum electrode was used as an auxiliary electrode and a calomel electrode was used as reference electrode with mild steel coupons.
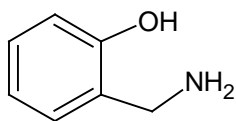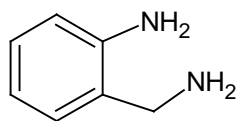
2-(aminomethyl)phenol   2-(aminomethyl)aniline

IH(I)   IH(II)

Results and Discussion

The corrosion rates of mild steel without and with inhibitors at 60^0C, 70^0C and 80^0C temperatures and 5mM concentration of inhibitors were determined by equation1in presence of H_2SO_4.

$$K \text{ (mmpy)} = 87.6 \text{ W} / \text{D A t} \qquad (1)$$

where W = weight loss of test coupon expressed in gm, A = Area of test coupon in square centimeter, D = Density of the material in gm/cm^3.

The surface coverage area and inhibition efficiency of metal were determined by 2 and equation3.

θ (surface coverage area) = $(1 - K / K_o)$ \qquad (2)

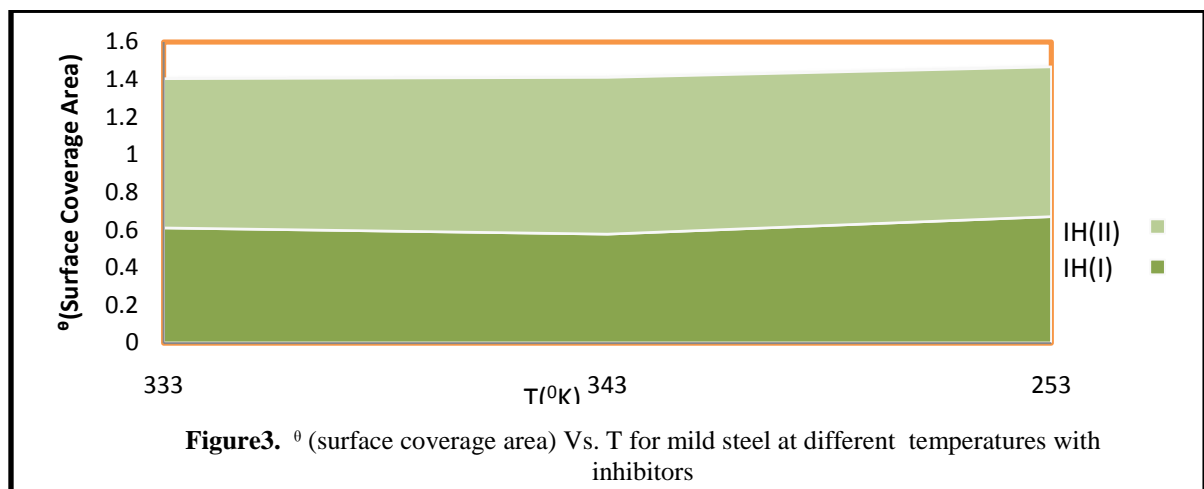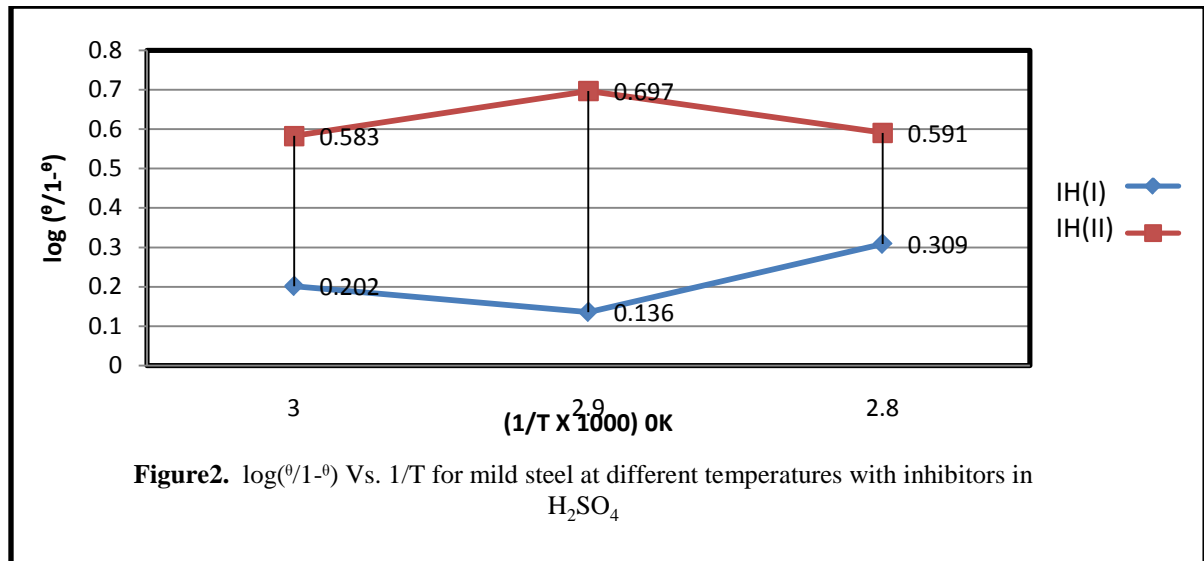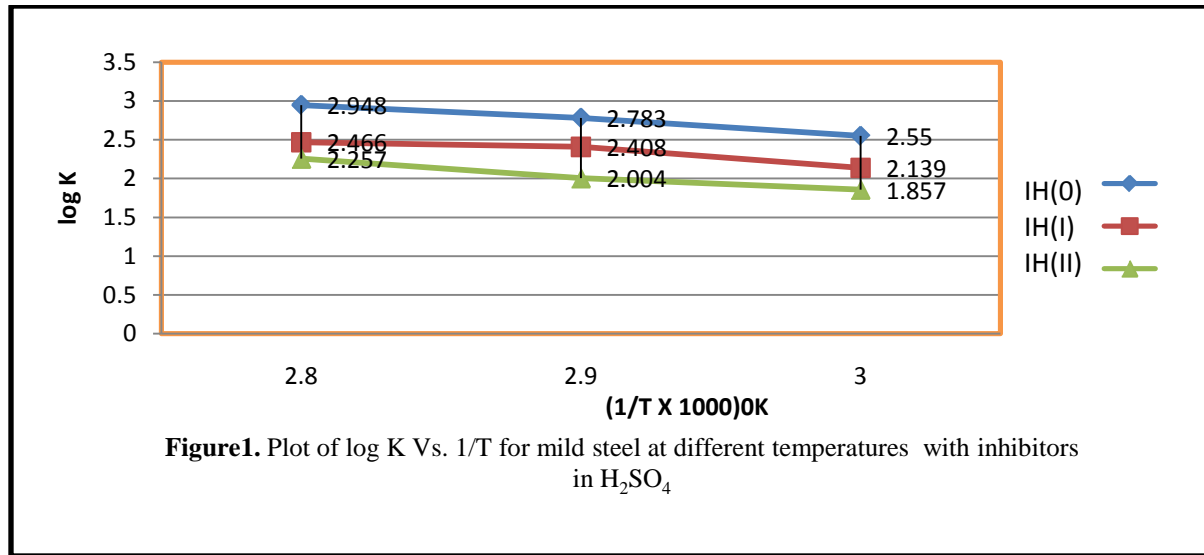where θ = Surface coverage area, K_o = corrosion rate without inhibitor K = corrosion rate with inhibitor

IE (Inhibition efficiency) = $(1- K / K_o)$ X 100 \qquad (3)where K_o is the corrosion rate without inhibitor,
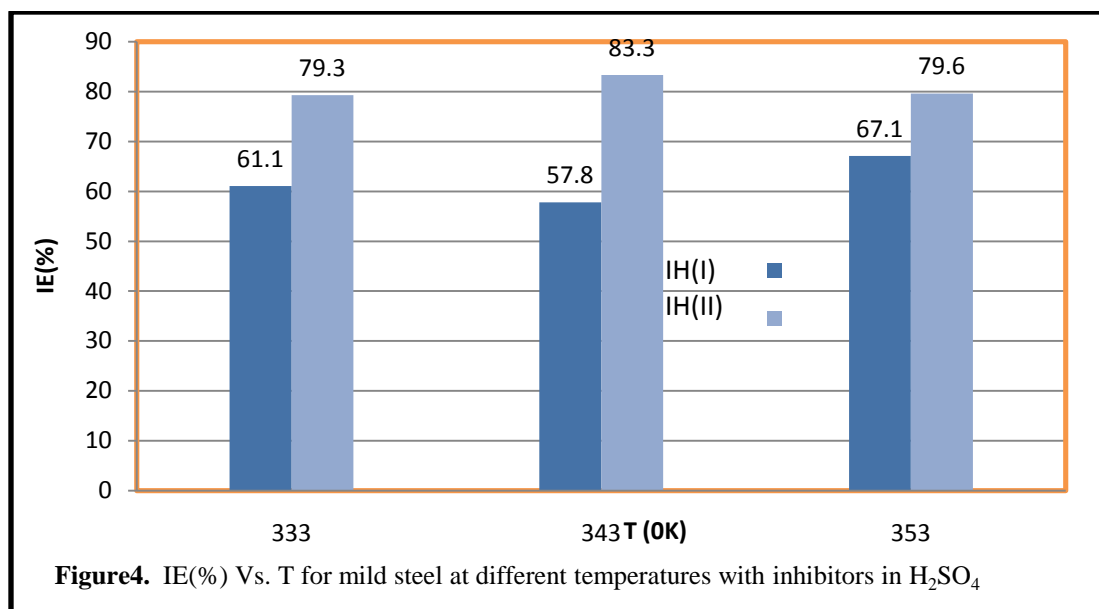
K = corrosion rate with inhibitor

The corrosion rates of mild steel, surface coverage area and inhibition efficiencies of 2-(aminomethyl)phenol and 2-(aminomethyl)anilinewere calculated by equation1, equation2 and equation 3 at different temperatures and 5mM concentration and these inhibitors values were mentioned in Table1. The results of Table1 were noticed that 2-(aminomethyl)anilinedecreased the corrosion rate of metal more with respect of 2-(aminomethyl)phenol. The surface coverage area and inhibition efficiency value found more with 2-(aminomethyl)aniline than that of2-(aminomethyl)phenol. The Plot of logK Vs. 1/T in figure1and log $(\theta/1- \theta)$ Vs.1/T in figure2 found to be straight line, these lines gave information about inhibitors adsorption. The plot between θ(surface coverage area) Vs. T in figure3 and IE(inhibition efficiency) Vs. T in fiure4 were shown inhibitors deposition on metal surface and its efficiencies at different temperatures.

Table1: Corrosion of mild steel at different temperatures in H_2SO_4medium in absence and presence of inhibitors

Inhibitors	Temperatures	60^0C	70^0C	80^0C	C (m M)
IH(0)	K_o	391	565	639	00
	$logK_o$	2.592	2.752	2.922	
IH(I)	K	118	192	330	5
	logK	2.071	2.283	2.518	
	$log(\theta/1-\theta)$	0.363	0.290	0.185	
	θ	0.698	0.661	0.605	
	IE (%)	69.80	66.10	60.50	
IH(II)	K	61	155	201	
	logK	1.785	2.191	2.303	
	$log(\theta/1-\theta)$	0.729	0.421	0.498	
	θ	0.843	0.725	0.759	
	IE (%)	83.30	72.50	75.9	

Figure1. Plot of log K Vs. 1/T for mild steel at different temperatures with inhibitors in H_2SO_4

Figure2. log(θ/1-θ) Vs. 1/T for mild steel at different temperatures with inhibitors in H_2SO_4

Figure3. θ (surface coverage area) Vs. T for mild steel at different temperatures with inhibitors

Figure4. IE(%) Vs. T for mild steel at different temperatures with inhibitors in H_2SO_4

The activation energy, heat of adsorption, free energy, enthalpy and entropy were calculated by equation4, equation5, equation6 and equation7 for inhibitors 2-(aminomethyl)phenol and 2-(aminomethyl)aniline, its values were recorded at 60^0C, 70^0C and 80^0C in Table2. The activation energy increased without addition of inhibitors and its values decreased after addition of inhibitors. It indicated that these inhibitors produced inhibition effect in H_2SO_4 environment. The results of heat of adsorption observed that inhibitors were boned with base metal by physical adsorption. Free energy and enthalpy values were shown that exothermic reaction occurred after addition of inhibitors. These results exhibited sign of adsorption between base metal and inhibitors. Theentropy values were mentioned in Table2 which indicated that deposition of inhibitors on the surface of metal in arranged way. Thermodynamical results of Table2 and its plot in figure5 noticed that inhibitors were formed complex with base metal.

$$d /dt (\log K) = E_a / R T^2 \qquad (4)$$

where T is temperature in Kelvin and E_a is the activation energy

$$\log (\theta/ 1-\theta) = \log (A .C) - (Q_{ads}/ R T) \qquad (5)$$

where T is temperature in Kelvin and Q_{ads} heat of adsorption

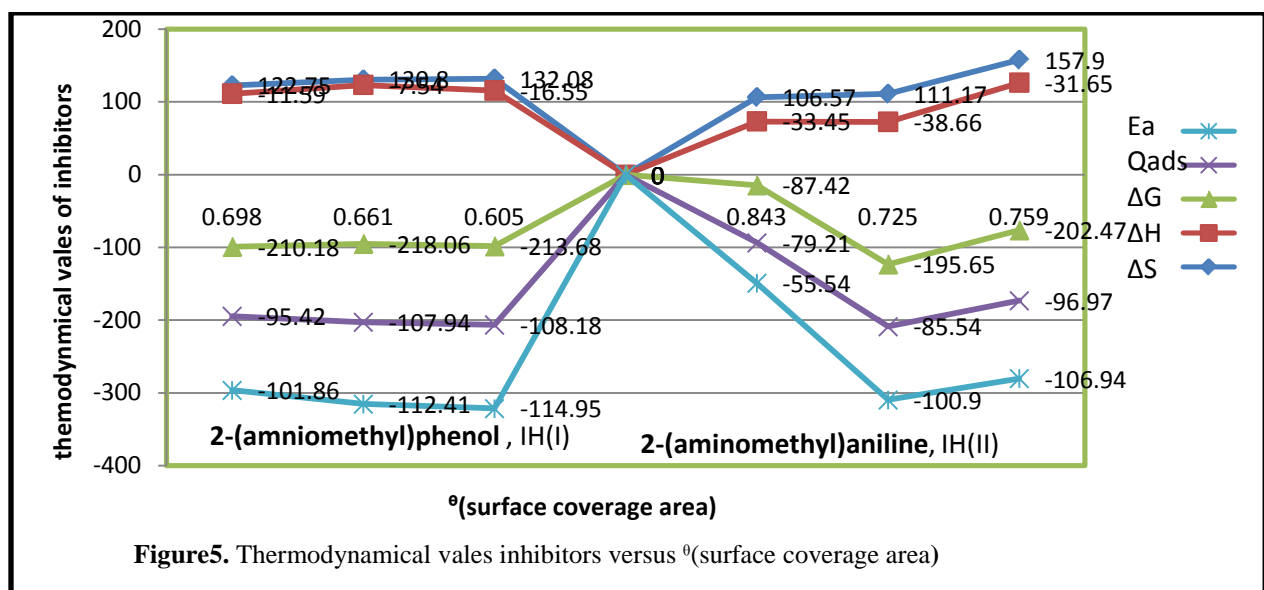$$\Delta G = -2.303 RT [\log C - \log (\theta/1-\theta) + 1.72] \qquad (6)$$

Where T is temperature in Kelvin and ΔG free energy

$$K = R T / N h \log (\Delta S^{\#}/ R) X \log (-\Delta H^{\#}/ R T) \qquad (7)$$

where N is Avogadro's constant, h is Planck's constant, $\Delta S^{\#}$ is the change of entropy activation and $\Delta H^{\#}$ is the change of enthalpy activation.

Table2. Thermodynamical values of inhibitors in H2SO4 medium for stainless steel

Inhibitors	Temperatures	60^0C	70^0C	80^0C
IH(0)	$E_a(o)(kJmol^{-1})$	146.34	154.39	157.90
IH(I)	$E_a(kJmol^{-1})$	122.75	130.80	132.08
	$Q_{ads.}$ $(kJmol^{-1})$	-11.59	-07.54	-16.55
	$\Delta G(kJmol^{-1})$	-210.18	-218.06	-213.68
	$\Delta H(kJmol^{-1})$	-95.42	-107.94	-108.18
	$\Delta S(JK^{-1})$	-101.86	-112.41	-114.95
IH(II)	$E_a(kJmol^{-1})$	106.57	111.17	157.90
	$Q_{ads.}$ $(kJmol^{-1})$	-33.45	-38.66	-31.65
	$\Delta G(kJmol^{-1})$	-87.42	-195.65	-202.47
	$\Delta H(kJmol^{-1})$	-79.21	-85.54	-96.97
	$\Delta S(JK^{-1})$	-55.54	-100.90	-106.94

Figure5. Thermodynamical vales inhibitors versus $^\theta$(surface coverage area)

The corrosion current density determined in the absence and presence of 2

-(aminomethyl)phenol and 2-(aminomethyl)aniline with the help of equation 8 and their values are recorded in Table3.

$$\Delta E/\Delta I = \beta_a \beta_c / 2.303 \, I_{corr} \, (\beta_a + \beta_c) \qquad (8)$$

where $\Delta E/\Delta I$ is the slope which linear polarization resistance (R_p), β_a and β_c are anodic and cathodicTafel slope respectively and I_{corr} is thecorrosion current density in mA/cm^2.

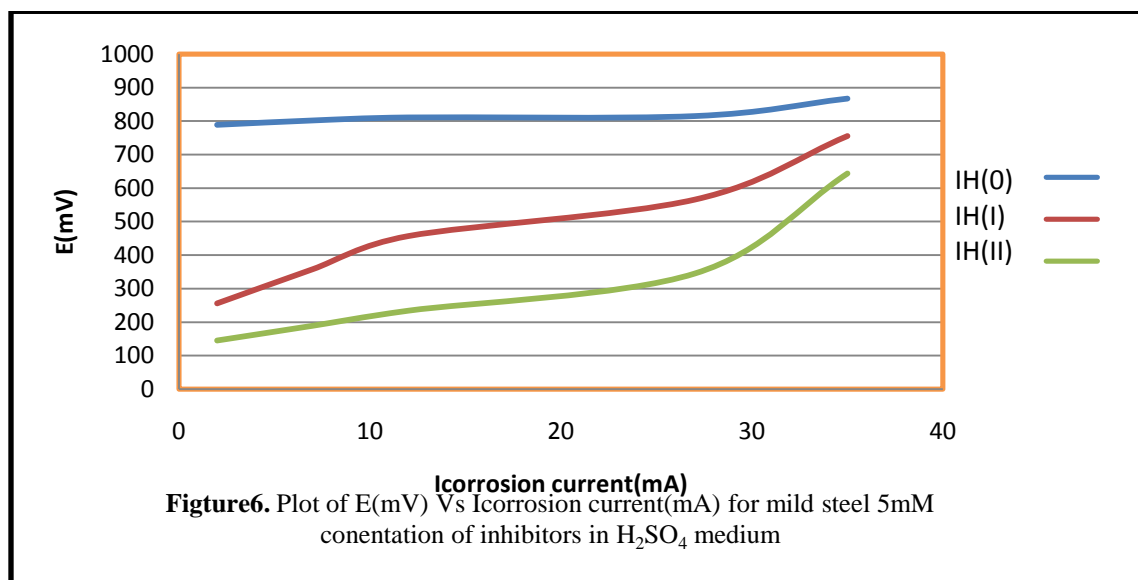The metal penetration rate (mmpy) was determined by equation9 in absence and presence of inhibitors.

$$C.\, R \, (mmpy) = 0.327 \, I_{corr} \, (mA \, /cm^2) \times Eq\,.Wt \, (g) \, / \, \rho \, (g/cm^3) \qquad (9)$$

where$I_{corr}$is the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight.

The results of Table3 indicated that corrosion current increased without inhibitors and it reduced with inhibitors and its values more decreased with 2-(aminomethyl)anilinewith respect of 2-(aminomethyl)phenol. Tafel graph was plotted in figure6 between electrode potential and corrosion current density in the absence and presence of inhibitors. Anodic potential, current density and corrosion rate increased without inhibitors but after addition of inhibitors cathodic potential and corrosion current increased and corrosion rate decreased and inhibition efficiency increased. The gravimetric results and potentiostat results were shown equality hence these inhibitors had good inhibitive effect in H$_2$SO$_4$meduim.

Table3. Potentiostatic polarization of mild steel with inhibitors in H$_2$SO$_4$

ΔE(mV)	ΔI	β_a	β_c	$I_{corr.}$	K(mmpy)	C (mM)
-815	405	320	205	27.73	228	0.00
-705	245	141	251	12.90	105	5
-610	165	110	285	7.65	67	

Figture6. Plot of E(mV) Vs Icorrosion current(mA) for mild steel 5mM conentation of inhibitors in H$_2$SO$_4$ medium

Conclusion:

Experimental results were collected by different sources of gravimetric and potentiostatfor inhibition effect of 2-(aminomethyl)phenol and 2-(aminomethyl)aniline in H_2SO_4 medium like corrosion rate without and with inhibitors, surface coverage areas and inhibition efficiencies, they indicated that these inhibitors produced anticorrosive effect. The results of activation energy, heat of adsorption, free energy, enthalpy and entropy were shown that used inhibitors were adhered with metal surface through complexation.

Acknowledgement:

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