

Study of Corrosion and Corrosion Protection of Stainless Steel in Phosphate Fertilizer Industry

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Abstract Phosphate industries use bulk amount of concentration H_2SO_4 during production of phosphate fertilizers. Stainless steel is major supporting metal for completion of several processing operational works. This acid produces corrosive effect for stainless steel. It develops corrosion cell on the surface of base metal and it changes its internal morphology as well as physical, chemical, mechanical properties. H_2SO_4 behaves like diabetes for this industrial metal and industries face economical. The eradication of corrosion problems used organic inhibitors like 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine and its inhibition effect and surface coverage area studied at different temperatures $333^{\circ}K$, $343^{\circ}K$ and $353^{\circ}K$ in presence of 15% H_2SO_4 and 15mM concentration of inhibitors. The corrosion rate of metal was determined by weight loss experiment and potentiostat techniques. The surface adsorption and surface thin film formation were analyzed by application of activation energy, heat of adsorption, free energy, enthalpy and entropy. The inhibition efficiencies and surface coverage areas were shown that the used inhibitors produced anticorrosive effect in acidic medium.

Keywords: stainless steel, inhibitors, weight loss, potentiostat, surface coverage area

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1. Introduction

The Corrosion of metal is not fully control but its effect can be minimized by application suitable methods e.g. give proper design and shape of operational metals [1], take care of surrounding operating temperatures and atmosphere [2], used different types of coatings [3], addition of inorganic and organic inhibitors as cathodic and anodic protection [4] and applied nanocoating [5]. When operational equipments came in contact of acidic environment [6], they exhibited several types of corrosion problems like galvanic, pitting crevice, stressed, intergranular, blistering, embrittlement. Different types of coatings methods used for corrosion alleviation of metal such coatings were metallic coating [7], inorganic coating [8], organic coating [9], painting coating, polymeric coating, and nanocoatings [10]. These coating did not provide good support for metal in acidic environment because porosities were developed on the surface of base metal during coatings. The H^+ ions entered into porosities of coating materials by the process of diffusion and it developed corrosion cell on the surface base metal.

Various types of inhibitors like inorganic, organic and mixed types used to control the corrosion of metal. Organic inhibitors which possessed nitrogen, oxygen, sulphur, silicon, phosphorous, methyl, phenyl, primary, secondary and tertiary alkyl groups whereas these organic compounds have high electron rich functional groups and

they have capacity to produce thin film on surface of metal. Inhibitors were bonded with metals by physical-chemical adsorption. Aromatic and heterocyclic organic compounds containing above mentioned functional groups produced anticorrosive effect in acidic medium.

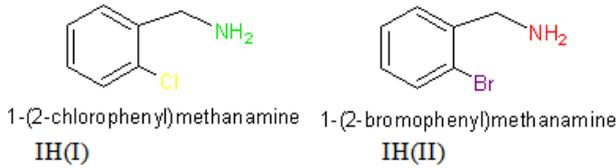
Nanocoating of $Zn_3(PO_4)_2$ [11], $Mg_3(PO_4)_2$ [12] and $AlPO_4$ [13] in presence of DLC (diamond like carbon) controlled high temperatures corrosion and minimize hydrogen ions attack. Plasma and composite coating gave corrosion protection of metal in acidic environment. Inhibitor 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine used for this work. These inhibitors contained electron rich functional which minimize the attack of H^+ ions and forming thin film and it also increased surface coverage area and efficiency. The thermodynamical results noticed that these inhibitors have good adsorption capability.

2. Experimental Procedure

Stainless steel coupons were cut into size of $(5 \times 3) \text{ cm}^2$. 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. Test sample dipped into 250ml biker with support glass hook and corrosion rate metal determined absence and presence of inhibitors 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine at different temperatures $333^{\circ}K$, $343^{\circ}K$ and $353^{\circ}K$ and 15mM concentration and

thermostat used to mention temperature. The corrosion rate was measured by gravimetric method.

The corrosion current density and corrosion rate 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 stainless steel coupons. The used inhibitors structure mentioned as:



3. Results and Discussion

The corrosion rates of stainless steel without and with inhibitors 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl) methanamine were determined by equation 1 and its results were mentioned in Table 1.

$$K(\text{mmpy}) = 87.6W / DA \quad (1)$$

where W = weight loss of test coupon expressed in gm, A = Area of test coupon in square centimeter, D = Density of the material in g/cm³.

The surface coverage areas (θ) and the inhibition efficiencies (IE) occupied by inhibitors were calculated equation 2 and 3 and their results were also written in Table 1.

$$\theta = (1 - K / K_o) \quad (2)$$

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

$$IE = (1 - K / K_o) \times 100 \quad (3)$$

where K_o is the corrosion rate without inhibitor, K = corrosion rate with inhibitor

Table 1. Corrosion of stainless steel at different temperatures without and with inhibitors in 15% H₂SO₄

Inhibitors	Temperatures	333 ^o K	343 ^o K	353 ^o K	C (m M)
IH(0)	K _o	391	565	836	00
	logK _o	2.592	2.752	2.922	
	K	118	192	230	15
IH(I)	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	
	K	61	155	201	15
	logK	1.785	2.191	2.303	
IH(II)	log($\theta/1-\theta$)	0.729	0.421	0.498	
	θ	0.843	0.725	0.759	
	IE (%)	84.30	72.50	75.90	

The results of Table 1 observed that corrosion rate increased in acidic medium without addition of inhibitors but its values decreased after addition of addition of inhibitors. The results of surface coverage area and inhibition efficiency with 1-(2-chlorophenyl)methanamine and 1-(2-bromophenyl)methanamine enhanced at different temperatures and it looked in Figure 1 plot between θ (surface coverage area) versus T^oK and Figure 2 IE (inhibition efficiency) versus T^oK. These results indicated that used inhibitors produced anticorrosive effect against acid.

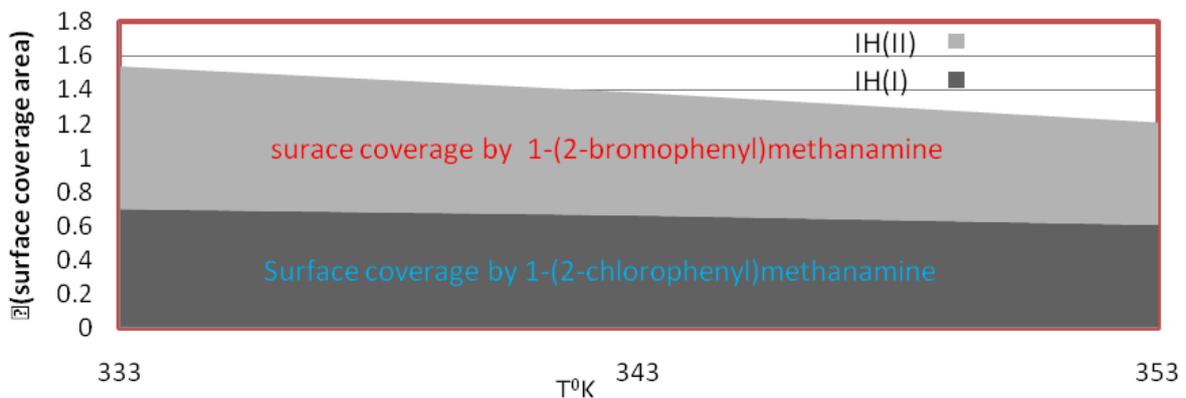


Figure 1. θ (surface coverage area) versus T^oK for stainless steel at different temperatures

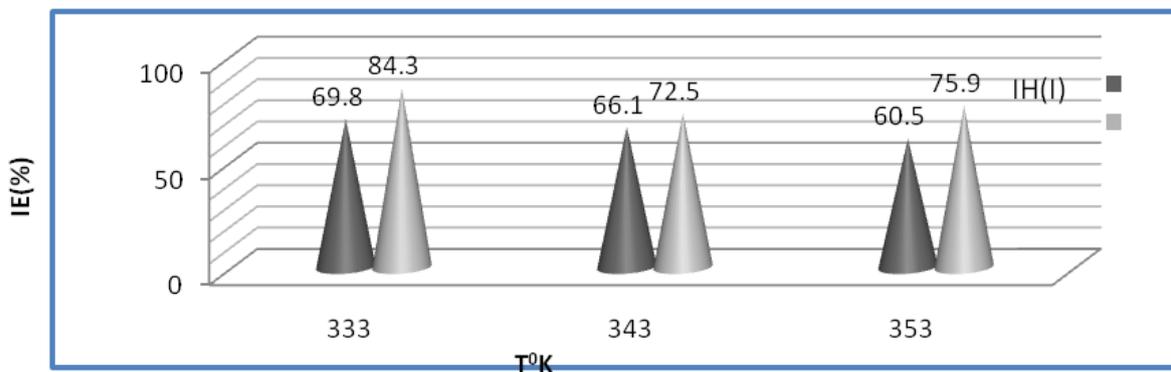


Figure 2. IE(%) versus T^oK for stainless steel at different temperatures

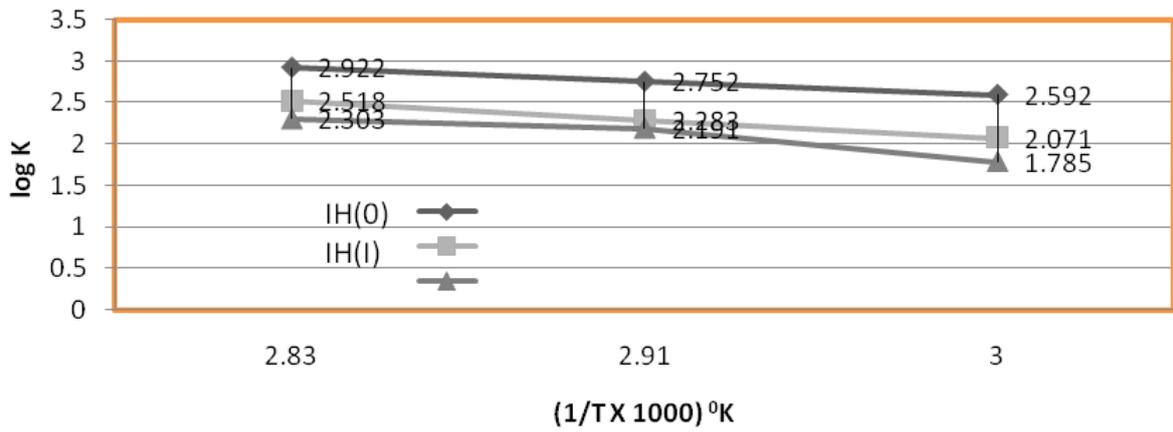


Figure 3. log K versus 1/T for stainless steel at different temperatures

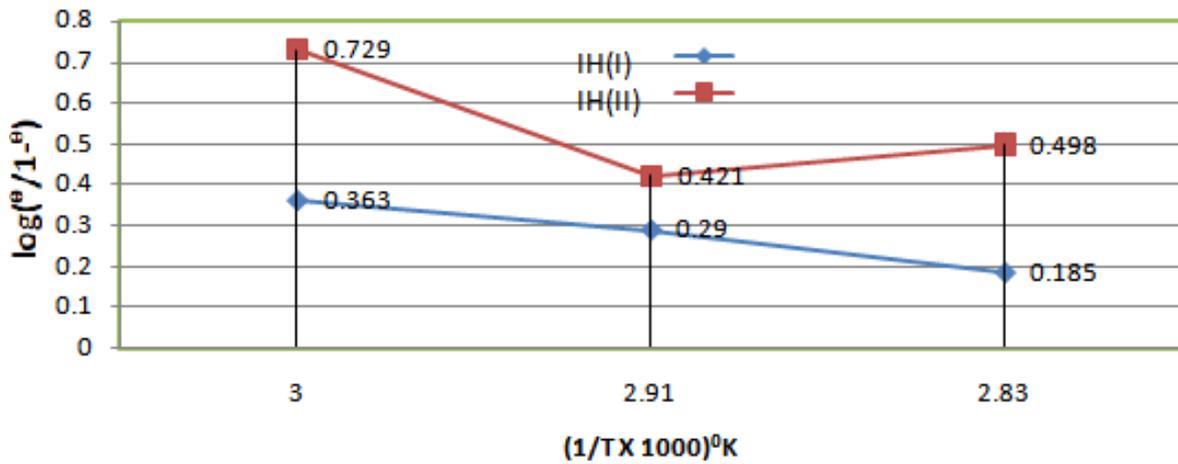


Figure 4. log(θ/1-θ) versus 1/T for stainless steel at different temperatures

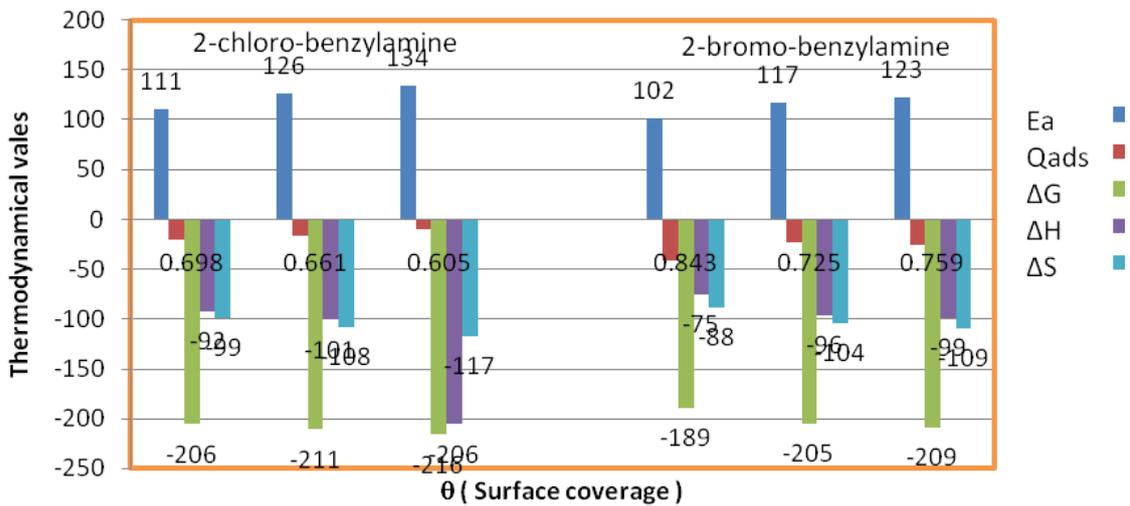


Figure 5. Thermodynamical values of different inhibitors versus θ(surface coverage area) at different temperatures

The activation energy, heat of adsorption, free energy, enthalpy and entropy of inhibitors 1-(2-chlorophenyl)methaneamine and 1-(2-bromophenyl)methaneamine were calculated by equation 4, equation 5, equation 6 and equation 7 and their values were recorded in Table 2. The activation energy increased without inhibitors and its values decreased with inhibitors and its values were determined by plot of logK versus 1/T in Figure 3. It indicated that inhibitors bonded with base metal. Heat of adsorption found to be negative which indicating that inhibitors adhered with metal by physio-

chemio adsorption. Its values were calculated by plot of log(θ/1-θ) versus 1/T in Figure 4. The results of free energy, enthalpy and entropy values were shown negative sign which depicted that adsorption occurred on the surface of metal and the graph of all thermodynamical values (Ea, Q_{ads}, ΔG, ΔH and ΔS) versus θ (surface coverage area) were presented in Figure 5 .

$$d/dt(\log K) = E_a / RT^2 \tag{4}$$

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

$$\log(\theta/1-\theta) = \log(A \cdot C) - (Q_{\text{ads}}/RT) \quad (5)$$

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

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

where T is temperature in Kelvin and ΔG free energy

$$K = R T/N h \log(\Delta S^\# / R) \times \log(-\Delta H^\# / R T) \quad (7)$$

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.

Table 2. Thermodynamical values of inhibitors in 15% H₂SO₄ for stainless steel

Inhibitors	Temperatures	333 ^o K	343 ^o K	353 ^o K
IH(0)	$E_a(o)(\text{kJmol}^{-1})$	148	153	157
	$E_a(\text{kJmol}^{-1})$	118	126	134
	$Q_{\text{ads}}(\text{kJmol}^{-1})$	-21	-16	-10
	$\Delta G(\text{kJmol}^{-1})$	-206	-211	-216
	$\Delta H(\text{kJmol}^{-1})$	-92	-101	-206
IH(II)	$\Delta S(\text{JK}^{-1})$	-99	-108	-117
	$E_a(\text{kJmol}^{-1})$	102	117	123
	$Q_{\text{ads}}(\text{kJmol}^{-1})$	-42	-23	-26
	$\Delta G(\text{kJmol}^{-1})$	-189	-205	-204
	$\Delta H(\text{kJmol}^{-1})$	-75	-96	-99
	$\Delta S(\text{JK}^{-1})$	-88	-104	-109

The corrosion current density determined in the absence and presence of inhibitor with the help of equation 8 and their values were recorded in Table 3.

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

where $\Delta E/\Delta I$ is the slope which linear polarization resistance (R_p), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is the corrosion current density in mA/cm².

The metal penetration rate (mmpy) was determined by equation 9 in absence and presence of inhibitors.

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

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

The results of Table 3 indicated that corrosion current increase without inhibitors and its values reduced after addition of inhibitors because these inhibitors enhanced cathodic current so corrosion current and corrosion rate minimized. Tafel graph was plotted in Figure 6 between electrode potential and corrosion current density in the absence and presence of inhibitors.

Table 3. Potentiostatic polarization of inhibitors in 15mM concentration and 15% of H₂SO₄

$\Delta E(\text{mV})$	ΔI	β_a	β_c	$I_{\text{corr}}(\text{mA/cm}^2)$	K(mmpy)	C(mM)
-650	550	350	250	55.79	4.379	0.00
-600	475	225	315	45.17	0.354	15
-575	350	175	325	30.10	0.236	

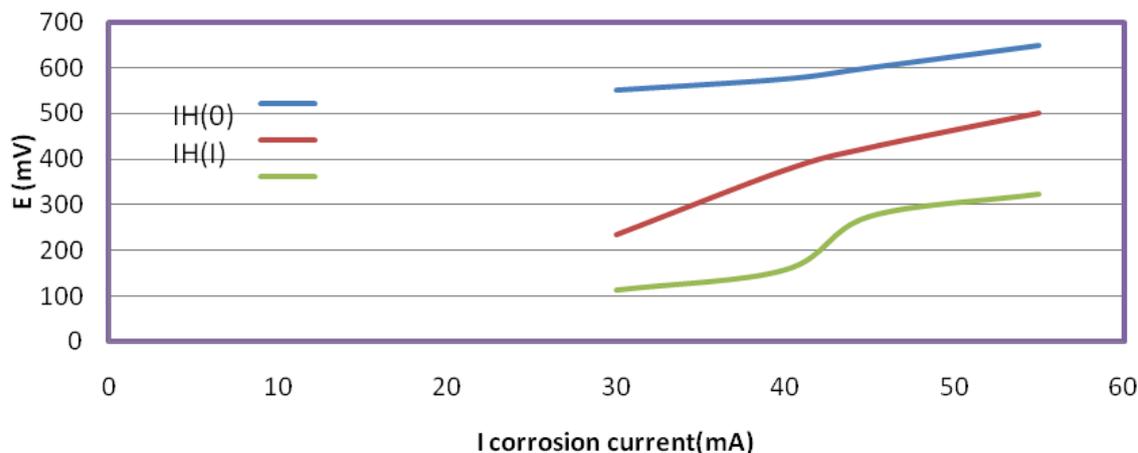


Figure 6. Plot of E (mV) Vs. I (mA) for stainless steel with 15mM concentration of inhibitors

4. Conclusion

These inhibitors possessed electron releasing functional which had capability to enhance electron charge density towards corroded metal and protected base metal by formation of thin film. The results of surface coverage area and inhibition efficiency for both inhibitors indicated that both inhibitors adhered with the surface of metal. The results of activation energy, heat of adsorption, free energy, enthalpy and entropy were shown both inhibitors bonded with base metal physical-chemical adsorption.

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