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Research Article

STUDYING CORROSION INHIBITORY EFFECT OF *ALOE VERA* JUICE ON STAINLESS STEEL USED FOR ORANGE JUICE STORAGE

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ABSTRACT

Stainless steel used in most of the applications of orange juice like recovery, processing and transportation. Orange juice is acidic nature. When it is kept in stainless steel container, it develops corrosion cell on the surface of metal. The electrochemical reaction occurs on the surface of metal and deterioration of metal starts. The harmful metal ions go into solution of orange juice which produces diseases in human being. *Aloe vera* juice is applied for the corrosion protection of stainless steel in orange juice environment. *Aloe vera* is natural product which is ecofriendly with human being. Its inhibition efficiency is studied at different concentrations and temperatures. For this work the concentrations of inhibitors were selected as 2ml, 4ml and 6ml and that concentration temperature was maintained at 20^0C, 25^0C, 30^0C and 35^0C. The percentage inhibition efficiency occured between 21 to 66. The surface coverage area increased with rise of temperatures. The corrosion rate was determined with help of weight loss and potentiostaic polarization methods. Surface adsorption phenomenon studied with application Langmuir isotherms and Temkin equation. Inhibition activities of *Aloe vera* were studied by the using activation energy, heat of adsorption, free energy, enthalpy and entropy. Experimental results showed that the inhibitor adheres with thin film on the surface of metal. The physical adsorption occurs between metal and inhibitor.

Key Words: *Aleovera, Orange Juice, Corrosion Cell, Physical Adsorption*

INTRODUCTION

Stainless steel is very useful material for engineering application. Its application is very wide in fruit juice areas. The corrosion of metals leads not only to the loss of metals but it is often the case of ecological catastrophes which occurs due to the destructions. Scientists developed several methods for the corrosion protection of materials. One of the most known methods of decreasing of metals corrosion rate is the use of organic and inorganic inhibitors. Most known inhibitor refer to noxious and toxic compounds and theirs using deteriorate ecological situation. Therefore, it is necessary to develop methods of selecting inhibitors which metals corrosion rate and are not harmful for environment. This metal is sensitive to acid and its destruction starts in presence acidic environment. Chemists use various types of inhibitors for corrosion protection metal. Several works have been done with help of organic and inorganic materials for the corrosion protection of metal (Mobin, 2008; Singh, 2010 and Alam *et al.,* 2009). Oixdes of metals and phosphate of metals used as inhibitors. Sulpha drugs (Wang *et al.,* 2008 and Brodinov *et al.,* 2007) gave good results for corrosion control of stainless steel in sugar industry. Aromatic amine Alam *et al.,* (2008) and Kalendova *et al.,* (2008) fused aromatic amine and hetero cyclic aromatic amine worked as inhibitors in phosphate inhibitors. Cyclic amine used for corrosion inhibition (Nmai, 2004 and Singh, 2011) of metal in pulp and paper industry. Nanocoatings of organic and inorganic on surface of metal could produced good inhibition properties and improve life of material. Several types of Nanocoatings can be done on the surface of materials like nanocomposite thin film coating, thermal barrier coating, Top layer coating, nanostructural change and conversion coating. Thiourea (Singh, 2009 and Singh, 2009) and its derivates worked as inhibitors in petroleum industry in various operational units like production, storage and transportation. Recently natural products applied for corrosion protection of metal in acidic medium and these inhibitors were found ecofriendly for environment. Metallic and nonmetallic coating mitigated affect of corrosion in corrosive environment. Organic compounds (Alam *et al.,* 2008) having nitrogen, oxygen and sulphur behave likes anticorrosive inhibitors. Electron rich organic compounds have good inhibition capability against acid. The corrosion is controlled by the application of aliphatic and aromatic amines (Kalendova *et al.,* 2008). It is also observed that primary, secondary, tertiary and quaternary amine produce good inhibitive effect against acidic medium (Nmai, 2004). Several workers used heterocyclic compounds as inhibitors which possessed nitrogen, oxygen and sulphur. Rubber, polymer and silicon are used as coating material (Singh, 2009 and Singh 2009) for protection of metal. For this work *Aloe vera* is used as inhibitors for corrosion of protection of stainless steel in orange juice.

MATERIALS AND METHODS

Stainless steel coupons of (5× 3) square meter shape and size were taken and ruffed with emery paper to increase the fineness of the coupons and then the coupons were washed with double distilled water and finally degreased with acetone and dried with air dryer. The tested coupons were dipped into 400ml solution of orange juice in 500ml beakers. Tests were performed at different concentrations 2ml, 4ml and 6ml *Aloe vera* and at different temperatures 20^{o}C, 25^{o}C, 30^{o}C and 35^{o}C and temperature were maintained constant by keeping the solutions in a thermostat. Potentiostaic polarization studies are carried out by using an EG and G Princeton Applied Research Model 173 Potentiostate. A platinum electrode is used as an auxiliary electrode and a calomel electrode is used as reference electrode.

RESULTS AND DISCUSSION

The Corrosion rate of metal was calculated in the absence and presence of inhibitors by equation1 and its value were given in Table1, Table3 and Table 5.

$$K\ (mmpy) = 13.56\ W / D\ A\ t \quad \ldots\ldots (1)$$

Where W = weight loss of test coupon expressed in kg, A = Area of test coupon in square meter, D = Density of the material in kg. M^{-3}

The inhibition efficiency and surface coverage area were calculated by the corrosion rate by using equation 2 and 3 its values depicted in Table 1, Table3 and Table5.

$$IE = (1- K / K_o)\ 100 \quad \ldots\ldots (2)$$

Where K is the corrosion rate with inhibitor and K_o is the corrosion rate without inhibitor. The surface coverage area may be written as:

$$\theta = (1 - K / K_o) \quad \ldots\ldots (3)$$

Where θ = Surface area, K = Corrosion rate with inhibitor, K_o = corrosion rate without inhibitor.

Table 1: Inhibition of Aloevera on stainless steel in orange juice at different temperatures and 2ml concentration

Inhibitor	Temp	20^{0}C	25^{0}C	30^{0}C	35^{0}C	C (ml)	logC
IH(0)	K_0	0.312	0.578	0.715	0.924	0.00	0.00
	$logK_0$	-0.505	-0.238	-0.145	-0.034		
	K	0.217	0.427	0.559	0.711		
	logK	-0.663	-0.369	-0.252	-0.148		
	θ	0.300	0.260	0.210	0.230		
IH(1)	(1- θ)	0.700	0.740	0.790	0.770	2	-2.69
	log(θ/1- θ)	-0.360	-0.450	-0.560	-0.520		
	(C/ θ)	-8.960	-10.350	-12.800	-11.690		
	log(C/ θ)	-0.017	-0.455	0.096	-0.161		
	IE (%)	30	26	21	23		

Aloe vera Inhibition activity studied at 2ml, 4ml and 6ml concentrations and at different temperatures 20^{o}C, 25^{o}C, 30^{o}C and 35^{o}C. The rate of corrosion of inhibitors at different concentrations and temperatures were recorded in Table 1, Table 3 and Table 5. Investigation of results of Table 1, Table 3 and Table 5 it observed that the concentration of inhibitors increased the corrosion rate of metal decreased and inhibition efficiency and surface coverage area increased.

Table 2: Thermodynamically parameters for Aloevera at different temperatures and 2ml concentration

Thermodynamically Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	32.94	15.25	9.15	2.11
E_a	47.75	35.11	23.35	17.65
Q_{ads}	-23.48	-28.83	-35.35	-32.32
∆G	-26.17	-31.52	-38.04	-35.01
∆H	-77.62	-57.03	-48.60	-41.03
∆S	-45.52	-34.04	-29.45	-25.24

Table 3: Inhibition Aloevera on stainless steel in orange juice at different temperatures and 4ml concentration

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.312	0.578	0.715	0.924	0.00	0.00
	$\log K_0$	-0.505	-0.238	-0.145	-0.034		
IH(1)	K	0.185	0.285	0.426	0.519	4	-2.39
	logK	-0.732	-0.548	-0.370	-0.284		
	θ	0.410	0.510	0.400	0.430		
	(1- θ)	0.590	0.490	0.600	0.570		
	log(θ/1- θ)	-0.158	-0.017	-0.176	-0.123		
	(C/ θ)	-5.820	-4.680	-5.970	-5.510		
	log(C/ θ)	-0.096	-0.167	0.013	-0.292		
	IE (%)	41	51	40	43		

Table 4: Thermodynamically parameters for Aloevera at different temperatures and 4ml concentration

Thermodynamically Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	32.94	15.25	9.15	2.11
E_a	43.75	30.11	20.35	15.65
Q_{ads}	-9.78	-10.83	-11.35	-7.32
∆G	-12.17	-3.47	-13.51	-10.04
∆H	-82.19	-68.57	-55.65	-49.12
∆S	-48.20	-40.93	-33.66	-30.24

Table 5: Inhibition of *Aloe vera* on stainless steel in orange juice at different temperatures and 6ml concentration

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.312	0.578	0.715	0.924	0.00	0.00
	$logK_0$	-0.505	-0.238	-0.145	-0.034		
IH(1)	K	0.152	0.198	0.323	0.426	6	-2.23
	logK	-0.818	-0.703	-0.452	-0.370		
	θ	0.520	0.660	0.530	0.540		
	$(1-\theta)$	0.480	0.340	0.470	0.460		
	$\log(\theta/1-\theta)$	0.034	0.288	0.052	0.069		
	(C/θ)	-4.280	3.370	4.200	4.120		
	$\log(C/\theta)$	-0.550	-0.430	0.690	-0.920		
	IE (%)	52	66	53	54		

Table 6: Thermodynamically parameters for Aloevera at different temperatures and 6ml concentration

Thermodynamically Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	32.94	15.25	09.15	02.11
E_a	53.36	45.05	28.53	23.01
Q_{ads}	-07.78	-17.94	-03.35	-05.32
ΔG	-04.18	-20.17	-05.38	-08.04
ΔH	-88.06	-78.82	-63.76	-54.71
ΔS	-51.64	-47.05	-38.64	-33.67

The plot between log (θ/1- θ) vs. log C is found to be straight line which indicates Langmuir adsorption isotherm in figure1. The graph between log (C/ θ) vs. log C is observed a straight line which indicates Temkin isotherm in figure 2. Figure 3 shows that the concentration of *Aloe vera* is enhanced then inhibition efficiency is also increased.

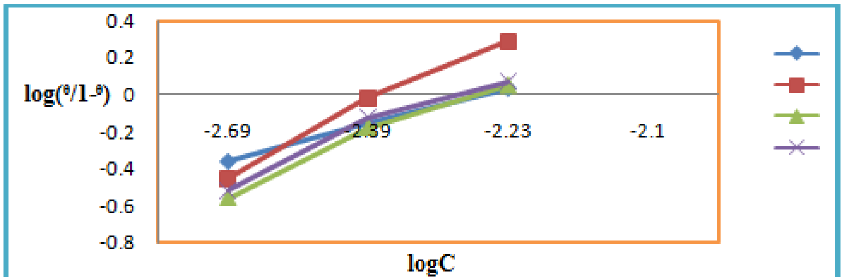

Figure 1: log (θ/1-θ) Vs log C for Stainless steel at different concentrations

The analysis of inhibitors action at different temperatures it noticed that at lower temperature inhibitors produced good inhibition efficiency and surface coverage area with respect of higher temperature which mention in Table 1, Table 3 and Table 5.

Activation energy was determined with help of Arrhenious equation 4

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

Where T is temperature in Kelvin and E_a is the activation energy of the reaction.

It values recorded in Table2, Table4 and Table6 without and with inhibitors. The plots between logK vs. 1/T found to be straight line in figure4 and with help of figure4 activation energy values were calculated.

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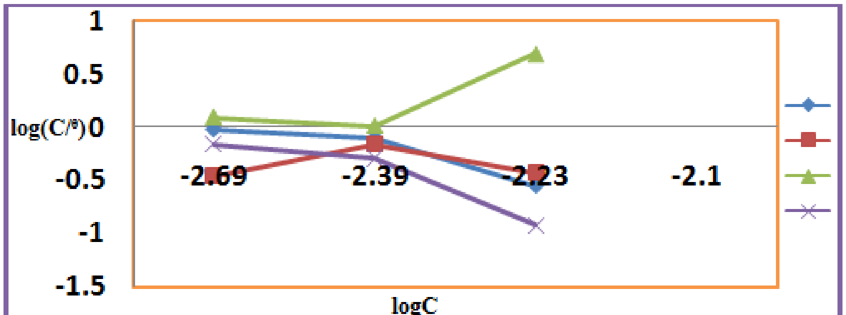

Figure 2: log(C/θ) Vs logC for Stainless steel at different concentrations

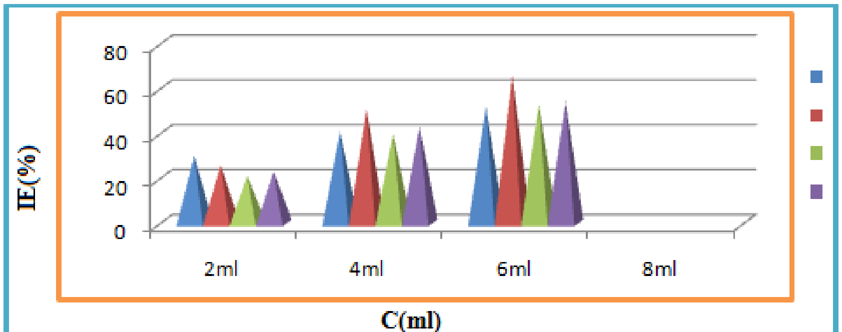

Figure 3: IE (%) Vs C (ml) for Stainless steel at different concentration

The activation energy results recorded in Table 2, Table 4 and Table 6 indicating that without inhibitors its values decreased and with inhibitors it values increased. These results confirmed that inhibitors were adhered to metal by physical adsorption.

The heat of adsorption was calculated by Langmuir adsorption isotherm equation and it values recorded in Table 2, Table 4 and Table 6.

$$\log (\theta/1-\theta) = \log (A.C) - (Q_{ads}/RT) \qquad \text{……..………… (5)}$$

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

The heat of adsorption found to be negative so it indicated that adsorption occurred on the metal surface. The values of heat of adsorption were shown that inhibitors were bind with metal by physical adsorption. It values were calculated with help of figure 5 with presence.

Study the effect of temperature it indicates that as temperatures increase, the inhibition efficiency is also enhance. This trend is shown in figure 6. Figure 7 plot between surface coverage area ($^{\theta}$) and temperature (T^0K) shows that the rise of temperatures, surface coverage area is increased.

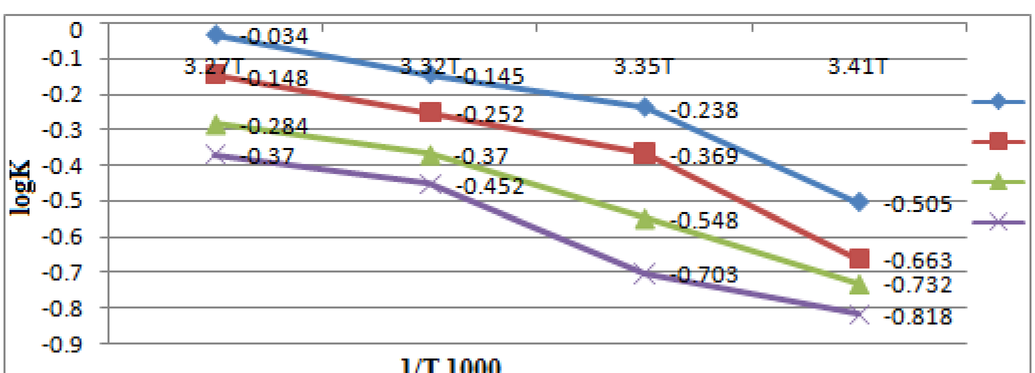

Figure 4: Plot of logK Vs. 1/T for Stainless steel at different temperatures

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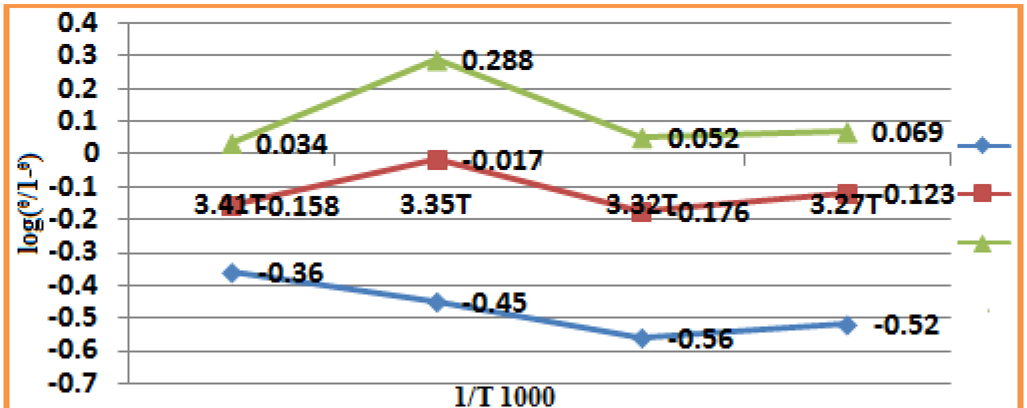

Figure 5: Plot of log(θ/1-θ) Vs. 1/T for Stainless steel at different temperatures

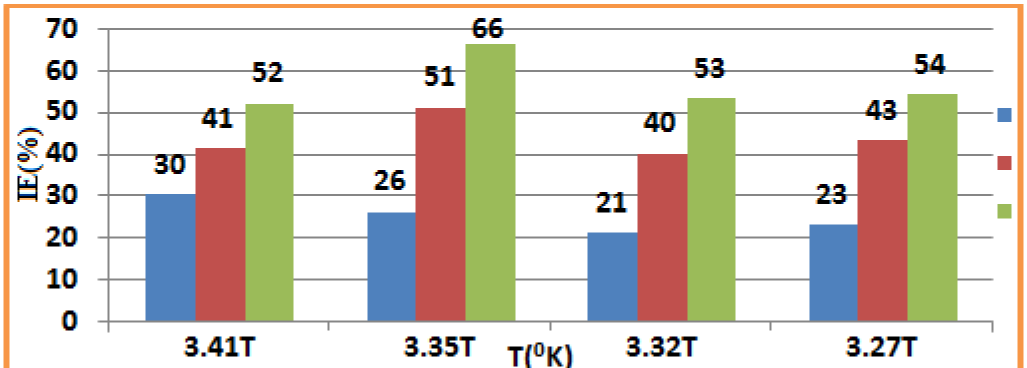

Figure 6: Plot of log K Vs T (0K) for Stainless stel at different temperatures

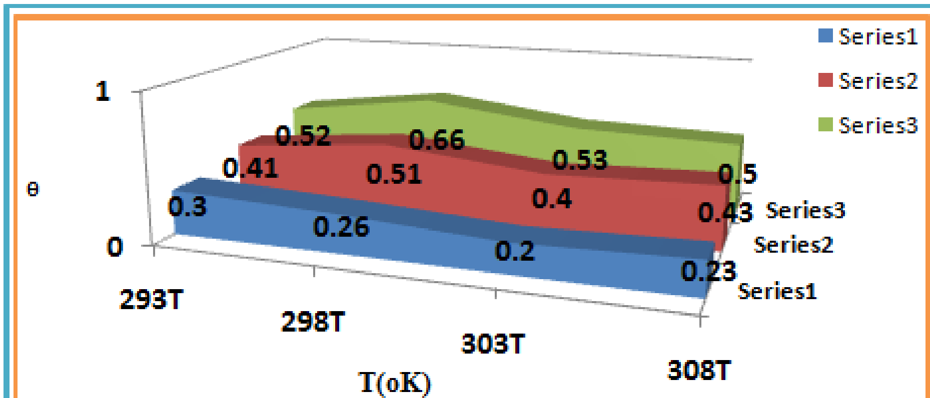

Figure 7: θ Vs T for Stainless steel at different temperatures

The energy of enthalpy and entropy were determined by transition state equation 6 and it values mentioned in Table 2.

$$K = R\,T / N\,h \log (\Delta S^{\#} / R) \times \log (-\Delta H^{\#} / R\,T) \quad \ldots\ldots\ldots\ldots\ (6)$$

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.

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Enthalpy energy fine to be negative, it observes that exothermic reaction happens between metal and inhibitors. The negative values of entropy indicate that inhibitors lose some degree of freedom during surface adsorption.
Free energy was determined by equation 7 and it values recorded in Table 2.

$$\Delta G = -2.303RT\ [\log C - \log(\theta/1\text{-}\theta) + 1.72] \ldots\ldots\ldots\ldots\ldots\ldots.. (7)$$

The negative sign of free energy shows that an exothermic reaction occurs between metal and inhibitors. Analysis of results of all thermodynamically parameters Table 2, Table 4 and Table 6 it seemed that adsorption reaction occurred on the surface of metal.
The corrosion rate and corrosion current density determined by potentiostaic technique with of equation 8 and 9 and it values recorded in Table 7.

$$\Delta E/\Delta I = \beta_a\ \beta c\ /\ 2.303\ I_{corr}\ (\beta_a + \beta_c) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (8)$$

Where ΔE/ΔI is the slope which linear polarization resistance (Rp), $\beta_{a\text{ and }}\beta_c$ are anodic and cathodic Tafel slope respectively and I_{corr} is the $_{corrosion}$ current density in mA/cm^2.
The metal penetration rate (mmpy) is determined by

$$C.\ R\ (mmpy) = 0.1288\ I_{corr}\ (mA\ /cm^2) \times \text{Equation Wt (g)} / \rho\ (g/cm^3) \ldots\ldots\ldots\ldots.. (9)$$

Where I_{corr} is the corrosion current density ρ is specimen density and Equation Wt is specimen equivalent weight.
Figure 7 indicates that Tafel graph has plotted between electrode potential and current density and absence and presence of inhibitors. Anodic potential, current density and corrosion rate increased without inhibitors but addition of inhibitors these values decreased and inhibition efficiency increased.

Table 7: Potentiostaic Polarization study of Aloevera inhibition at different concentration on stainless steel in orange juice at 30^{0}C

Inhibitor	ΔE	ΔI	βa	βc	Icorr	K(mmpy)	IE (%)	C(ml)
	-800	350	250	230	28.81	0.875	0.00	0
IH(0)	-700	325	200	225	23.38	0.710	18.85	2
IH (1)	-650	300	175	200	18.75	0.569	34.97	4
	-600	275	150	180	16.30	0.495	43.2	6

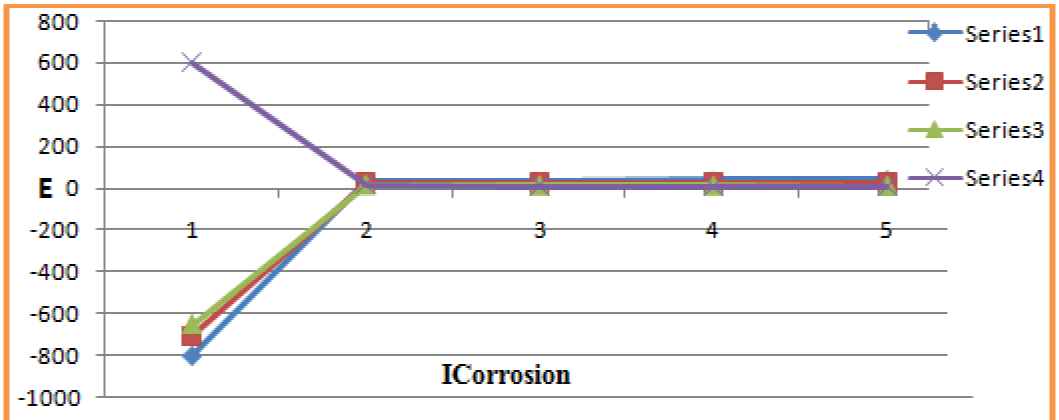

Figure 8: Plot of E (electrode potential) Vs. I(corrosion current) for Stainless steel

Conclusion

Thermodynamically values like activation energy, heat of adsorption, free energy, enthalpy and entropy show that inhibitors associate with metal through physical bonding.

The experimental results showed that upon addition of inhibitor corrosion rate is reduced. The inhibitor has corrosion controlling power at higher temperature.
The inhibitor produces thin surface film on interface of metal surface. The inhibitor has good Inhibition efficiency and Surface Coverage area and minimizes the attack of corrosive substance.

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