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Research Article

CORROSION PROTECTION OF MILD STEEL IN SUGAR INDUSTRY

***Rajesh Kumar Singh**
Department of Chemistry, Jagdam College, J P University, Chapra, India
**Author for Correspondence*

ABSTRACT
Most of the processing equipments of industries are made of mild steel. During processing of sugar various types of reactions are applied like sulphonation and carbonation. These reactions generate corrosive environment for mild steel in sugar industry. There are other corrosive substances are also available like O_2, NH_3, Cl^- , $SO_4{}^{2-}$ and boiling water. When mild steel comes in contact of corrosive environment, electrochemical cell is developed and oxidation of metal starts. Metallic equipments go through corrosive processes such as galvanic, pitting, stress, crevice, cracking etc. These corrosive processes reduce life of equipments and increase cost of production, sometimes causing major accidents. Organic inhibitors selected for this work is sulphanilamide, sulphapyridine and sulphathiazole. It is observed that these inhibitors have good anticorrosive activities in this corrosive environment. The experimental results notice that used inhibitors produce good inhibition efficiency and surface coverage area at different concentrations and temperatures. The rate of corrosion is determined with help of gravimetric and potentiostatic polarization technique.

INTRODUCTION
Mild steel is a very important industrial material because most of the industrial equipments are made of mild steel. It is economical and can be easily converts into desirable shapes and sizes. It is an economical metal so it is used in formation of technical equipments. This metal is sensitive to acid and its destruction starts in acidic environment. Several works have been done with help of organic and inorganic materials for the corrosion protection of metal[1-3]. For this work organic inhibitors[4, 5] have selected have good inhibition efficiency in acidic medium. Several works have been done with help of organic and inorganic materials for the corrosion protection of metal. Organic compounds [6] having nitrogen, oxygen and sulphur behave like anticorrosive inhibitors. Electron rich organic compounds have good inhibition capability against acid. The corrosion is controlled by the application of aliphatic and aromatic amines[7]. It is also observed that primary, secondary, tertiary and quaternary amine is produced good inhibitive effect against acidic medium[8]. Thiourea[9] and its derivatives are suitable inhibitors to minimize corrosion in acidic environments. Several workers used heterocyclic compounds as inhibitors which possessed nitrogen, oxygen and sulphur. Rubber, polymer and silicon are used as coating material[10, 11] for protection of metal. Ecofriendly organic inhibitors are used control corrosion in acidic medium. The surface adsorption phenomenon studied with help of thermodynamical parameters like activation energy (E_a), heat of adsorption (Q_{ads}), free energy (G), heat of enthalpy (H) and entropy(S). These thermodynamical values calculated with help of Arrhenius and Langmuir isotherm equation. Inhibitors surface adsorption activity investigated at different concentrations and temperatures.

MATERIALS AND METHODS
Mild steel coupons of ($3\times 2.5 \times 0.6$) 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 test solution was prepared by the addition of required amounts of AR grade H_2SO_4acid and the said inhibitors in double distilled water. The tested coupons were dipped into 400ml solution in 500ml beakers. Tests were performed at different concentrations 1mM, 5mM and 10mM and at different temperatures 30°C, 40°C, 50°C, 60°C and 70°C and temperature was maintained constant by keeping the solutions in a thermostat. Potentiostatic polarization studies are carried out by using an EG & G Princeton Applied Research Model 173

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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.

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

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 & 3 its values depicted in Table 1.

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

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:

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

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

Inhibitors sulphanilamide, sulphapyridine and sulphathiazole, inhibition activities studied at 1mM, 5mM and 10mM concentrations at these concentrations temperatures maintained 30^0C, 40^0C, 50^0C, 60^0C and 70^0C. The rate of corrosion of inhibitors at different concentrations and temperatures were recorded in Table1. Investigation of results of Table 1, it observed that the concentration of inhibitors increased the corrosion rate of metal decreased and inhibition efficiency and surface coverage area increased. 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. Show the figure 3 plot between percentage inhibition efficiencies IE (%) vs. different concentrations C (mM) indicates that as concentration increased inhibition efficiency and surface coverage also increased.

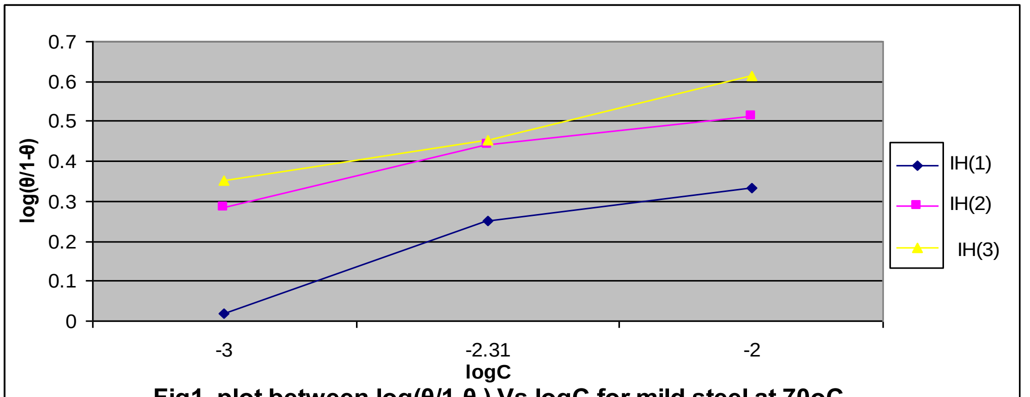

Fig1. plot between log(θ/1-θ) Vs logC for mild steel at 70oC temperature

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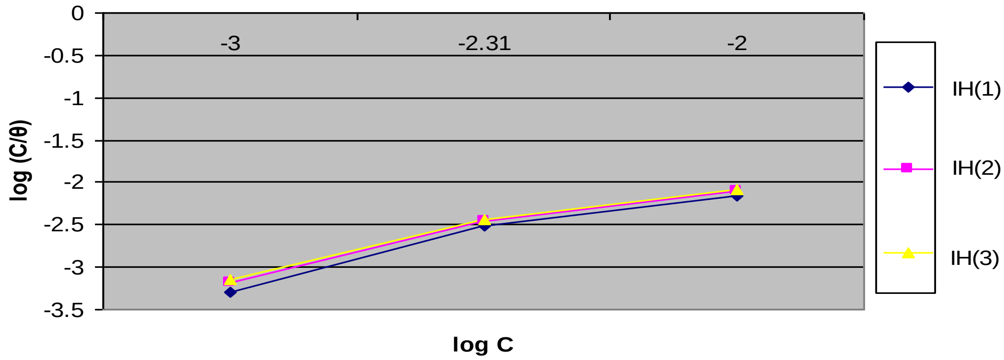

Fig. 2 Plot between log (C/θ) Vs log C for mild steel at 70oC temperature

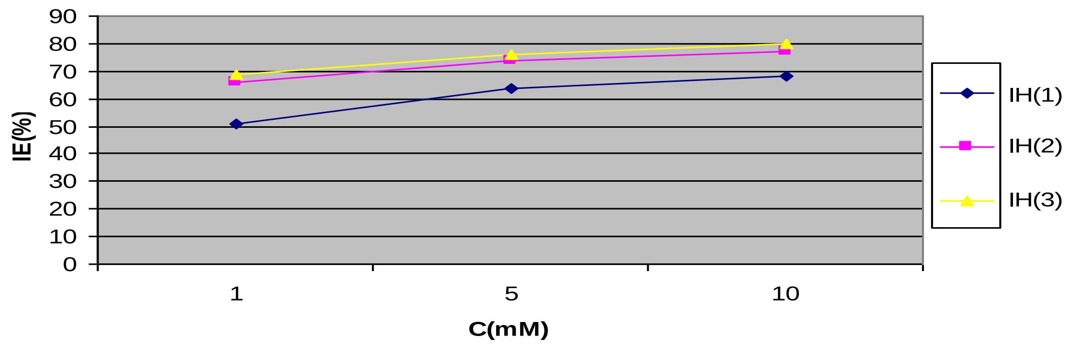

Fig.3.Plot between IE(%) Vs C(mM) for mild steel at 70oC temperature

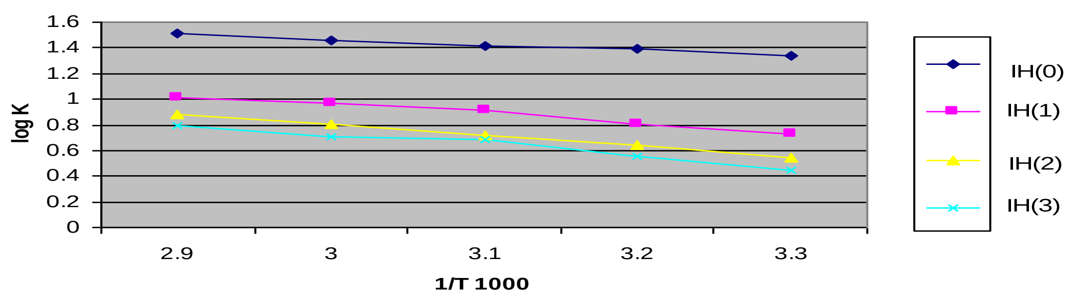

Fig.4 Plot between log K Vs 1/T 1000 for mild steel at 10mM concentration

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Table1. Inhibition of mild steel with different inhibitors at different concentrations and temperatures

Inhi	Temp	K	$logK_0$	K	logK	θ	log (θ/1- θ)	IE (%)	log(C/ θ)	C (mM)	log C
IH (1)	30^0C	22.344	1.349	8.344	0.921	0.626	0.223	62.6	-3.203	1	-3
	40^0C	24.803	1.394	9.461	0.975	0.618	0.208	61.8	-3.209		
	50^0C	26.419	1.421	10.716	1.030	0.594	0.165	59.4	-3.226		
	60^0C	29.268	1.466	13.727	1.137	0.530	0.052	53.0	-3.275		
	70^0C	32.373	1.510	15.850	1.200	0.510	0.017	51.0	-3.292		
	30^0C	22.344	1.349	6.623	0.821	0.703	0.374	70.3	-2.463	5	-2.31
	40^0C	24.803	1.394	7.798	0.891	0.685	0.337	68.5	-2.474		
	50^0C	26.419	1.421	9.256	0.966	0.649	0.266	64.9	-2.497		
	60^0C	29.268	1.466	10.206	1.008	0.651	0.270	65.0	-2.496		
	70^0C	32.373	1.510	11.647	1.066	0.640	0.249	64.0	-2.503		
	30^0C	22.344	1.349	5.417	0.733	0.757	0.493	75.7	-2.120	10	-2
	40^0C	24.803	1.394	6.551	0.813	0.737	0.447	73.7	-2.132		
	50^0C	26.419	1.421	8.023	0.904	0.696	0.359	69.6	-2.157		
	60^0C	29.268	1.466	9.535	0.979	0.674	0.315	67.4	-2.171		
	70^0C	32.373	1.510	10.207	1.008	0.684	0.335	68.4	-2.164		
IH (2)	30^0C	22.344	1.349	5.813	0.764	0.739	0.452	73.9	-3.131	1	-3
	40^0C	24.803	1.394	6.280	0.797	0.746	0.467	74.6	-3.127		
	50^0C	26.419	1.421	7.577	0.879	0.713	0.396	71.3	-3.146		
	60^0C	29.268	1.466	9.114	0.959	0.688	0.343	68.8	-3.162		
	70^0C	32.373	1.510	11.044	1.043	0.658	0.284	65.8	-3.181		
	30^0C	22.344	1.349	4.735	0.674	0.788	0.570	78.8	-2.413	5	-2.1
	40^0C	24.803	1.394	5.129	0.710	0.793	0.583	79.3	-2.410		
	50^0C	26.419	1.421	6.634	0.821	0.748	0.472	74.8	-2.436		
	60^0C	29.268	1.466	7.687	0.885	0.737	0.440	73.7	-2.442		
	70^0C	32.373	1.510	9.536	0.979	0.705	0.378	70.5	-2.461		
	30^0C	22.344	1.349	3.498	0.543	0.843	0.729	84.3	-2.074	10	-2
	40^0C	24.803	1.394	4.396	0.643	0.822	0.664	82.2	-2.085		
	50^0C	26.419	1.421	5.362	0.729	0.797	0.593	79.7	-2.098		
	60^0C	29.268	1.466	6.412	0.806	0.780	0.549	78.0	-2.107		
	70^0C	32.373	1.510	7.591	0.880	0.765	0.512	76.5	-2.116		
IH (3)	30^0C	22.344	1.349	4.867	0.733	0.782	0.493	75.7	-3.106	1	-3
	40^0C	24.803	1.394	5.969	0.813	0.759	0.447	73.7	-3.119		
	50^0C	26.419	1.421	6.788	0.904	0.743	0.359	69.6	-3.129		
	60^0C	29.268	1.466	7.697	0.979	0.737	0.315	67.6	-3.132		
	70^0C	32.373	1.510	9.945	1.008	0.692	0.335	68.4	-3.159		
	30^0C	22.344	1.349	3.815	0.543	0.829	0.729	84.3	-2.391	5	-2.1
	40^0C	24.803	1.394	4.210	0.643	0.830	0.664	82.2	-2.390		
	50^0C	26.419	1.421	6.273	0.729	0.762	0.598	79.7	-2.428		
	60^0C	29.268	1.466	7.066	0.806	0.758	0.549	78.0	-2.430		
	70^0C	32.373	1.510	8.386	0.880	0.740	0.512	76.5	-2.440		
	30^0C	22.344	1.349	2.857	0.455	0.872	0.833	87.2	-2.059	10	-2
	40^0C	24.803	1.394	3.665	0.564	0.852	0.760	85.2	-2.069		
	50^0C	26.419	1.421	4.946	0.694	0.812	0.635	81.2	-2.090		
	60^0C	29.268	1.466	5.164	0.712	0.823	0.667	82.3	-2.084		
	70^0C	32.373	1.510	6.282	0.798	0.805	0.615	80.4	-2.094		

IH (0) without inhibitor, IH (1) sulphanilamide, IH (2) sulphapyridine, IH (3) sulphatiazole

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 and figure6. The observation of the effect of concentrations and temperatures in Table1 indicated that sulphathiazole has good inhibitive effect at higher temperature than that of sulphanilamide and sulphapyridine.

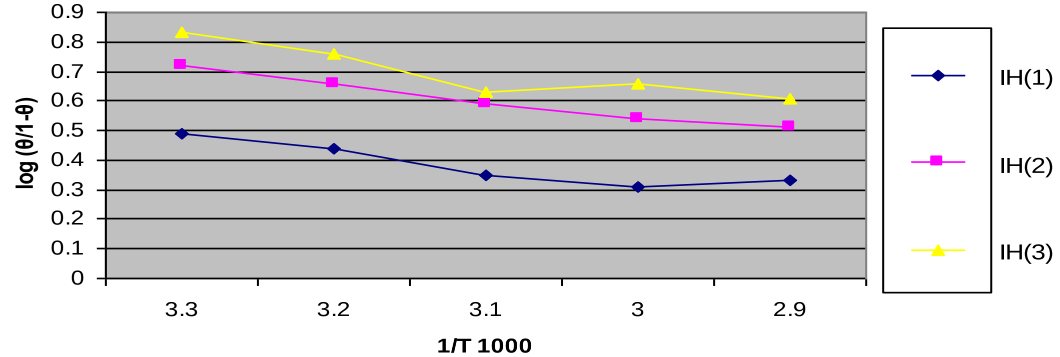

Fig.5 Plot between log (θ/1-θ) Vs 1/T for mild steel at 10 mM concentration

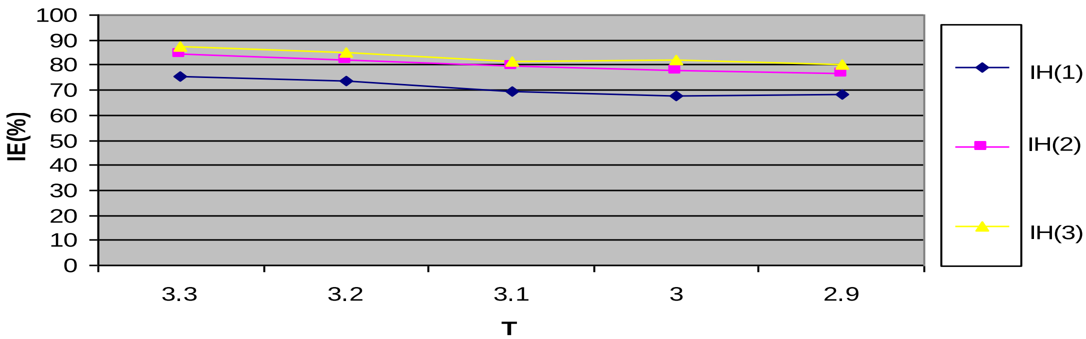

Fig.6 Plot between IE (%) Vs. T for mild steel at 10 mM concentration

Activation energy was determined with help of Arrhenious equation 4

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

where T is temperature in Kelvin and E_a is the activation energy of the reaction.
It values recorded in Table2 without and with inhibitors. The plots between logK vs. 1/T found to be straight line in fig.4 and with help of fig.4 activation energy values were calculated. The activation energy results recorded in Table 2 indicating that without inhibitors its values enhanced and with inhibitors it values reduced. These results conformed that inhibitors were adhered with metal by physical-chemical adsorption.
The heat of adsorption was calculated by Langmuir adsorption isotherm equation and it values recorded in Table 2.

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

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

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-chemical adsorption. It values were calculated with help of figure 5. It is noticed that the corrosion rate increase absence of inhibitors and decrease with presence of inhibitors.
The energy of enthalpy and entropy were determined by transition state equation 6 and it values mentioned in Table 2.

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

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.
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.

$$\Delta G = -2.303RT\,[\log C - \log (\theta/1-\theta) + 1.72] \qquad 7$$

The negative sign of free energy shows that an exothermic reaction occurs between metal
and inhibitors. Analysis of results of all thermodynamical parameters Table 2, it seemed that adsorption reaction occurred on the surface of metal.
The corrosion rate and corrosion current density determined by potentiostatic technique with of equation 8 and 9 and it values recorded in Table 3.

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

where $\Delta E/\Delta I$ is the slope which linear polarization resistance (Rp), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is the corrosion current density in $\mu A/cm^2$.
The metal penetration rate (mmpy) is determined by

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

Table2. Thermodynamical parameters for used inhibitors

Inh. Temp	30^0C	40^0C	50^0C	60^0C	70^0C
IH(0) E_a	85.16	86.13	84.26	84.13	83.77
IH(1) E_a	46.29	49.76	53.60	56.18	55.92
IH(2) E_a	34.27	39.36	43.23	46.25	48.81
IH(3) E_a	28.72	34.52	41.15	40.86	44.27
IH(1) Q_{ads}	-31.11	-27.36	-21.28	-18.07	-18.58
IH(2) Q_{ads}	-46.02	-40.64	-35.16	-31.50	-28.40
IH(3) Q_{ads}	-52.28	-46.52	-37.65	-38.27	-34.11
IH(1) ΔG	-267	-256	-243	-232	-226
IH(2) ΔG	-282	-269	-257	-246	-236
IH(3) ΔG	-289	-275	-259	-253	-241
IH(1) ΔH	-13.57	-18.85	-24.49	-28.80	-30.28
IH(2) ΔH	-1.57	-8.44	-14.11	-18.88	-23.18
IH(3) ΔH	-3.87	-3.61	-12.03	-13.48	-18.63
IH(1) ΔS	-80	-85	-103	-106	-88
IH(2) ΔS `	-86	-92	-87	-101	-89
IH(3) ΔS	-94	-91	-90	-95	-99

IH (0) without inhibitor, IH (1) sulphanilamide, IH (2) sulphapyridine, IH (3) sulphatiazole

where $I_{corr\ is}$ the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight. Tafel graph 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. Sulphapyridine and sulphathiazole produced good inhibition than that of sulphanilamide,.

Table3. Potentiostatic polarization of different inhibitors for Mild steel

Inhibitors	β_a (mV)	β_c (mV)	I_{cr} ($\mu A/cm^2$)	Corr. rate (mmpy)	IH (%)	
IH (0)		550	450	9.43	24.47	00.0
IH (1)	300	400	59.87	11.26	54.00	
IH (2)		250	300	27.86	8.58	65
IH (3)	200	250	20.67	6.37	74.00	

IH (0) without inhibitor, IH (1) sulphanilamide, IH (2) sulphapyridine, IH (3) sulphatiazole

The use inhibitors have possessed sulphathiazole functional groups whereas these functional groups have electron released capacity. When metal is oxidized by acid, these inhibitors donate electron toward metal and reduced corrosive effect. Sulphapyridine and sulphathiazole produce chelating effect so it show good inhibition efficiency whereas sulphanilamide forms intermolecular hydrogen bonding so it constructs a large molecule which covers more surface area by a thin film and its inhibition efficiency more than that of other two inhibitors. Thermodynamical values like activation energy, heat of adsorption, free energy, enthalpy and entropy show that inhibitors associate with metal through physical-chemical bonding.
Sulphanilamide, sulphapyridine and sulphatiazole have possessed electron releasing functional groups. The experimental results show that addition of inhibitor corrosion rate is reduced. These inhibitors have corrosion controlling power at higher temperature. Analysis of the values of all thermodynamical parameters indicate that inhibitors are occupied their position on the metal surface through physical adsorption.

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