

*Full Paper*

## **Corrosion Inhibition Effect of Substituted Quinoline and Its Condensation Products on Mild Steel in Acidic Media**

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**Abstract-** Corrosion inhibition of mild steel in 2N HCl medium in presence of newly synthesized organic compounds, 2-chloroquinoline-3-carbaldehyde (FQ), [(1Z)-(2-chloroquinoline-3-yl) methylene] hydrazone (FQMH), 2-6- Bis- {(2-chloroquinoline-3-yl-methylene}-amino}-hexanoic acid (FQHA) and (3Z)-4-(2-chloroquinoline-3-yl)-2-(mercapto methyl)but-3-enoic acid (FQBA) were investigated by weight loss and galvanostatic polarisation techniques. Effect of concentration, time of immersion and temperature effect on corrosion inhibition efficiency was evaluated. The inhibiting performances of all the compounds were found to increase with the increase in concentrations.

**Keywords-** Schiff base, Corrosion, Weight loss, Polarization

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### **1. INTRODUCTION**

Steel forms a major part of constructional material in many industries and logistical applications. The environment in which steel is put to use varies widely from acidic to alkaline to saline and humid conditions. The susceptibility of steel to corrosion under these conducive conditions has been thoroughly documented in monographs in the field of

corrosion science and engineering [1-4]. During the fabrication of steel, processes such as extrusion, calendaring of molten metal will be resorted to get either tubes or plates. Under these instances the steel surface gets oxidized and develops a mill scale measuring in micron level. Chemically the mill scale is iron oxide, which is highly refractory and thermal insulator. This behavior of mill scale is detrimental in situations where heat transfer between two fluids is to be ensured unhindered, akin to the one encountered in thermal power stations. During pre commissioning activities of boiler and other boiler accessories in thermal power stations the mill scale present on the heat transfer surfaces, will have to be removed through acid cleaning. This method of removing adherent scales using acids is termed as pickling in metallurgical operations [5]. Acid used in many plating industry as well as descaling processes involve HCl, H<sub>2</sub>SO<sub>4</sub> along with certain additives which includes inhibitors [6]. During acid cleaning of boiler tubes in thermal power station %5 HCl along with inhibitor and other additives will be admitted in to system at a temperature of 800 °C. A competitive reaction sets in between, the acid, which not only intend to remove mill scale but also exhibits tendency to eat indiscriminately the pristine bare metal and the inhibitor exhibiting propensity to bind on to bare metal surface preferentially. The rate at which the acid induced corrosion of bare metal and the rate at which the inhibitory protection offered insitu by inhibitor, will decide, the efficiency of the inhibitor, and hence the success of the whole operation.

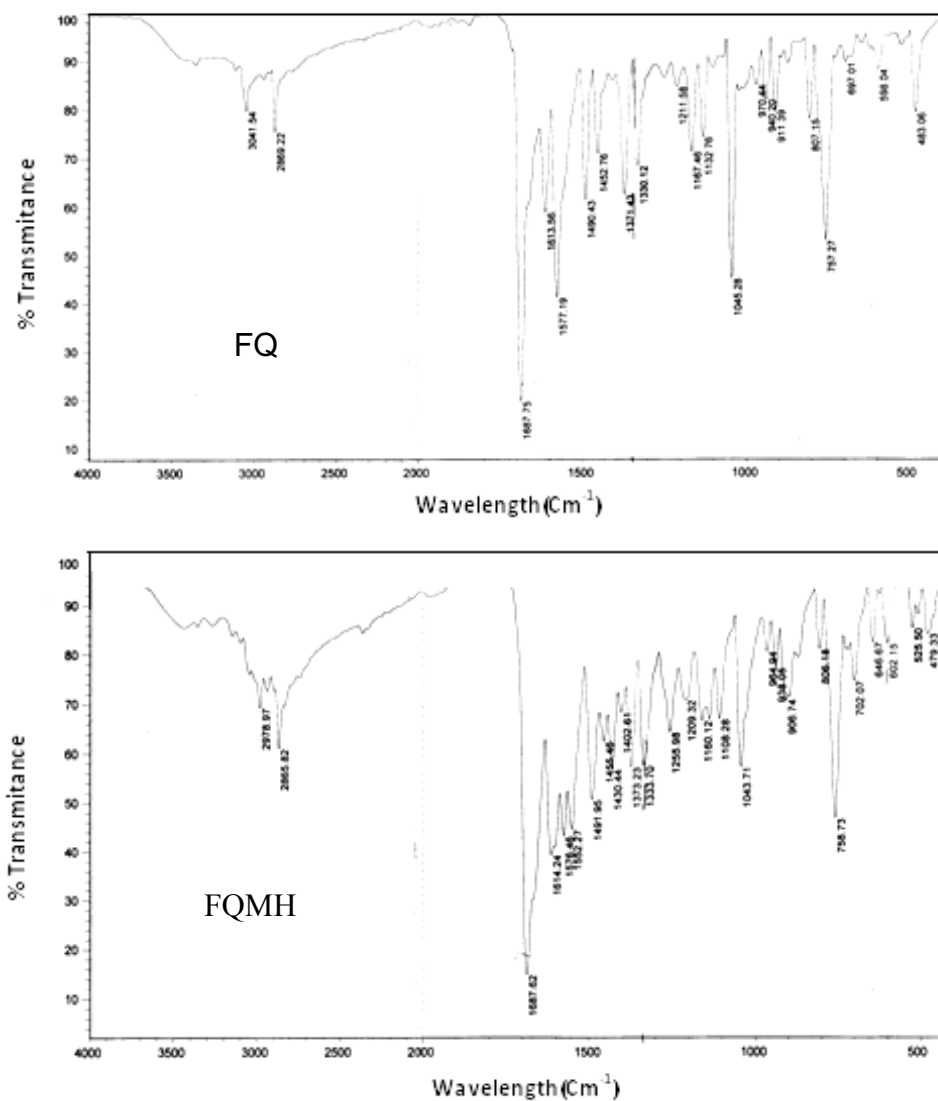
Quinolines and substituted quinolines find extensive use in analytical chemistry as chelating agents. This quality is being attributed to the presence of element N in the adjoining ring. The pre requisite for any molecule intended to be used as inhibitor is being satisfied by quinoline through the element N. Exploiting this structurally imbibed quality team of researchers led by Cicileo found that 8-hydroxy quinolines can inhibit corrosion in copper in neutral aqueous NaCl solution [7]. The synergistic participation of Ln<sup>+3</sup> salts with 8-hydroxy quinolines inhibits effectively the hydrochloric acid corrosion in Zinc. Through standard synthetic techniques 2-chloro-quinolines can be formulated to yield 2-chloro-3-formyl-quinolines. The formylation introduces a group which has pronounced chelating ability on the quinoline ring. The performances of the formyl quinolines as acid zone inhibitors under synergised conditions of chloride ions forms the scope of the present work.

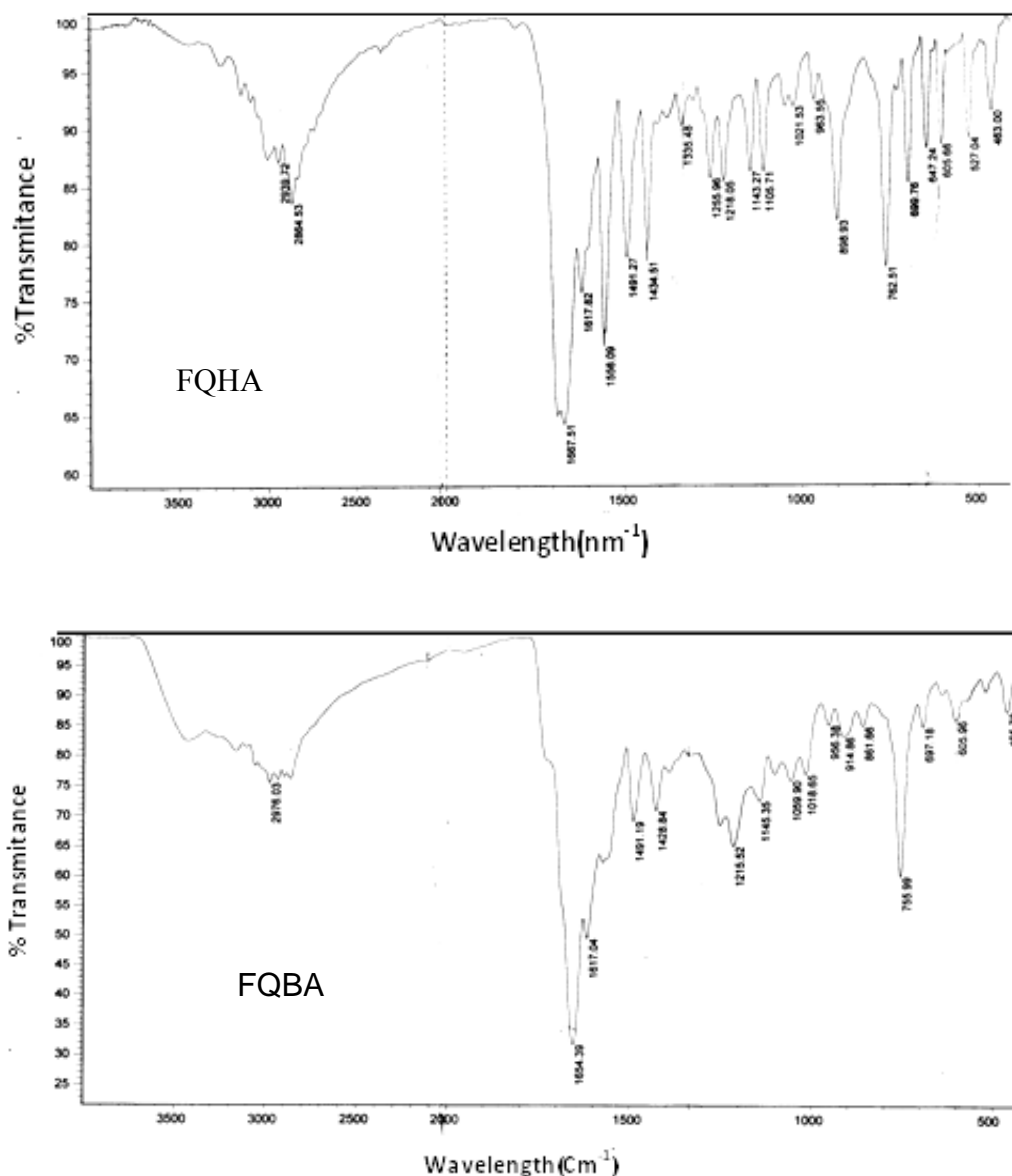
The present work involves the synthesis of condensation product between precursor 2-chloro-3-formyl-quinolines and aminoacids namely glycine, its homologue Lysine and Sulphur bearing Cystiene dihydrochloride. The compounds were later evaluated for the inhibition efficiency on mild steel in 2N HCl media through weight loss and galvanostatic polarisation techniques.

## 2. EXPERIMENTAL

### 2.1. Material preparation

The precursor 2-chloro-3-formyl-quinoline was synthesized as per the standard Wilsmeier method described elsewhere [8]. Throughout the synthesis of condensation products AR grade chemicals and demineralised water were used and standard literature was adopted for all the synthetic method [8]. The condensation products FQMH, FQHA and FQBA were synthesized by refluxing molar proportions of precursor 2-chloro-3-formyl-quinoline with glycine to get FQMH, Lysine to get FQHA and Cystiene di hydrochloride to get FQBA in presence of 0.5ml of conc  $H_2SO_4$  and solution maintained in 50ml absolute alcohol. The contents were refluxed gently for six hours before the reaction was quenched in ice water mixture. All the compounds were recrystallised in alcohol and characterized by spectral scanning. The chemical structures of the compounds are given in Table 1 and the corresponding IR spectra of the compounds are given in Fig. 1.





**Fig. 1.** FTIR spectra of the prepared compounds

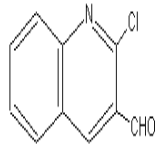
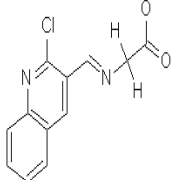
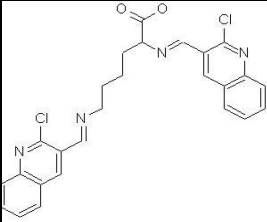
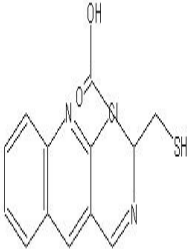
## 2.2. Weight loss measurements

Metal coupon were taken through all preparative cleaning method and final mirror finish for the surface was obtained by mechanical polishing through different grades of emery papers. Metal sample dimensions were 5×2×0.16 cm and their dimensions were measured before and after each experiment and area was calculated.

The condensation products having strength 200–800 ppm were dissolved in 25 mL polar solvent mixture containing DMF, DMSO and Alcohol in ratio of 3:1:1 and the solution was added to corroding medium. The strength of the corroding medium was adjusted to 2N HCl with demineralised water.

Pre weighed steel coupons were hung in above prepared schiff's base solution for 4hr and 8hrs at 303K under fully covered condition. A parallel observation without inhibitor compound was also made. Experiments were duplicated every time for concurrency.

**Table 1.** Structure of the inhibitor compounds

Name	Chemical structure	Abbreviation
2-chloro quinoline-3-carbaldehyde		FQ
[(1Z)-(2-chloro quinoline-3-yl) methylene] hydrazone		FQMH
2-6- Bis- {(2-chloro quinoline-3-yl-methylene)} -amino}-hexanoic acid,		FQHA
(3Z)-4-( 2-chloro quinoline-3-yl)- 2-(mercapto methyl)but-3-enoic acid,		FQBA

### 2.3. Polarisation studies

Polarisation studies were carried on 1cm<sup>2</sup> exposed area of mild steel coupon. A three-compartment cell of 125 mL capacity was used for carrying out experiment. Platinum electrode was used as auxiliary electrode, while standard calomel electrode (SCE) was used as reference electrode. The metal coupon formed the working electrode. For galvanostatic polarisation experiment metal surface preparation methods were followed on identical lines

to that of weight loss measurements. Corrosive medium containing different concentrations of inhibitor was prepared on the same lines as described in weight loss measurements. The corroding medium containing inhibitors was filled in three-compartment cell ensuring the expulsion of air bubble from the capillary tip. The working electrode was aligned with its exposed area lying very close to capillary tip.

A DC source (calibrator Rohnan make), which can provide a lowest current step of 10 micro amps, was used. Anodic and cathodic polarisation was established by reversing the polarities between Platinum electrode and working electrode. The polarisation data was collected by scanning between 0.01 mA to 15 mA in each cycle. Before reversing the polarity the exposed surface was mildly polished to remove corrosion debris. The cathodic polarisation was always started as first cycle followed by the anodic cycle. The open circuit potential, (OCP), was recorded after allowing sufficient time for the reading to stabilize.

#### **2.4. Elevated temperature studies**

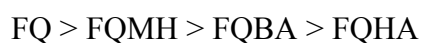
For knowing the thermo dynamic parameters as well as to know about the inhibiting efficiencies of the inhibitors at elevated temperatures polarisation studies of inhibitors at optimized concentrations were conducted at temperatures 303 K, 313 K and 323 K.

### **3. RESULTS AND DISCUSSIONS**

#### **3.1. Weight loss studie**

Weight loss observations were made on fabricated steel coupons by immersing in 200 mL of 2N HCl solution with and without inhibitor for known immersion time periods. The values of weight loss in grams per unit area and corrosion rate expressed in milli inches per year for the inhibitor compounds are reported in Table 2.

The inhibition efficiency was found to increase in general with the concentration though the effect of extended immersion time does not seem to have significant influence on the inhibition efficiencies. The order of inhibition efficiencies are given below,



This could be attributed to the presence of coordinating sites in the inhibitor molecule. The adsorption of the inhibitor molecule through the act of coordination with the metal surface will lead to formation of insulative layer around the substrate. The molecule FQ with a free carbonyl group could bind with less steric hindrance and hence the observed performance. The successive schiffs bases having been formed by utilizing the carbonyl group though brings in additional coordinating sites the steric hindrance could dissuade from adsorbing through a flaw less film.

**Table 2.** Corrosion parameters generated by weight loss measurements

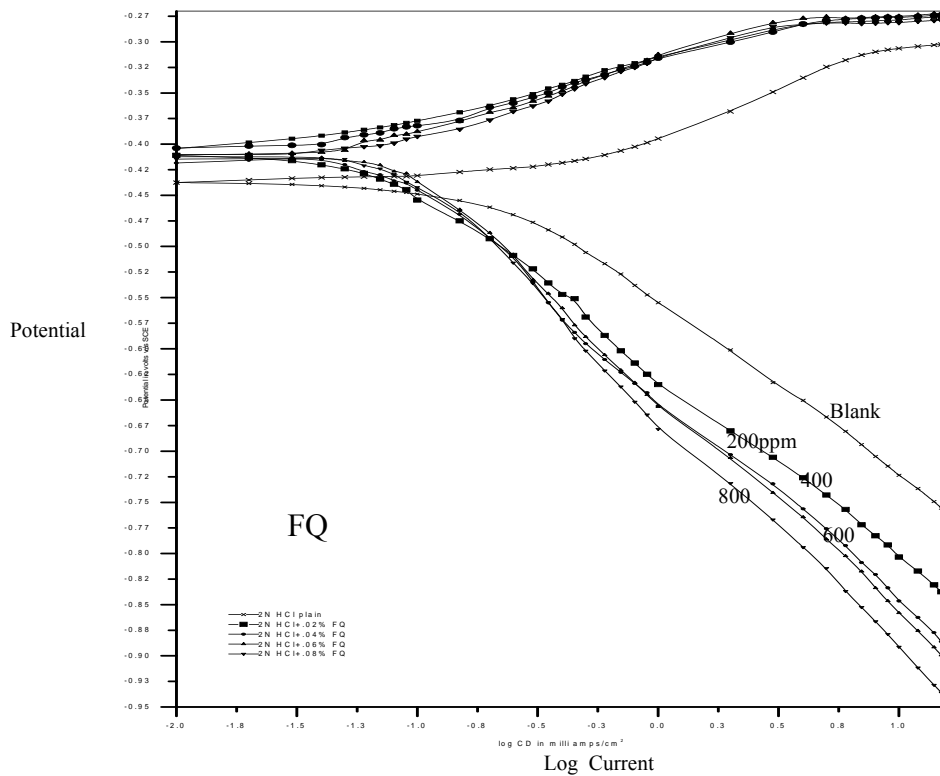
Inhibitor	Concentration	Time of immersion					
		4hr		8hr		% $\eta$	% $\eta$
		mpy	gpy	mpy	Gpy	4hr	8hr
Blank	ppm	0.049	2.49	0.045	2.27		
FQ	200	0.027	1.383	0.023	1.142	44	50
	400	0.018	0.945	0.019	0.936	62	59
	600	0.012	0.612	0.009	0.480	75	79
	800	0.008	0.424	0.008	0.437	81	83
FQMH	200	0.015	0.773	0.013	0.700	69	70
	400	0.014	0.750	0.010	0.766	70	74
	600	0.012	0.641	0.011	0.749	74	76
	800	0.013	0.613	0.010	0.459	75	77
FQHA	200	0.028	1.403	0.019	0.975	44	57
	400	0.020	1.038	0.016	0.806	58	64
	600	0.018	0.913	0.014	0.734	63	68
	800	0.015	0.735	0.012	0.634	66	69
FQBA	200	0.016	0.844	0.011	0.598	66	69
	400	0.016	0.812	0.013	0.669	67	71
	600	0.014	0.710	0.011	0.580	71	74
	800	0.013	0.690	0.010	0.764	72	75

mpy=milli inches per year and gpy=grams per year per cm<sup>2</sup>

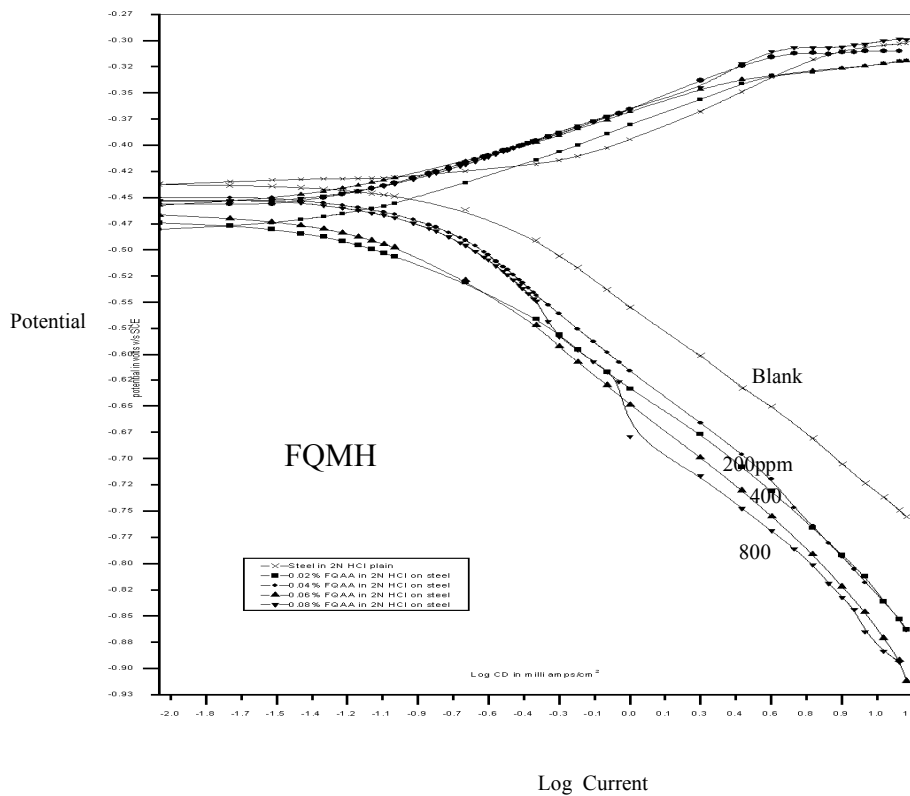
### 3.2. Polarization studies

The performances of the inhibitor compounds in 2N HCl media on mild steel coupons under artificially induced polarity through external DC source was evaluated over all concentrations as attempted during weight loss techniques and its polarization curves are given in Fig. 2-5. Various corrosion parameters such as corrosion density ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), Tafel slopes ( $b_a$  and  $b_b$ ) and inhibition efficiency (IE%) of FQ, FQMH, FQHA and FQBA were arrived through interpretation of Tafel curves the results are tabulated in Table 3.

It can be interpreted from the results contained in the table that the inhibition efficiencies of the compounds increase in general with the concentration. The values of the corrosion current decrease with the increase in inhibitor concentration.

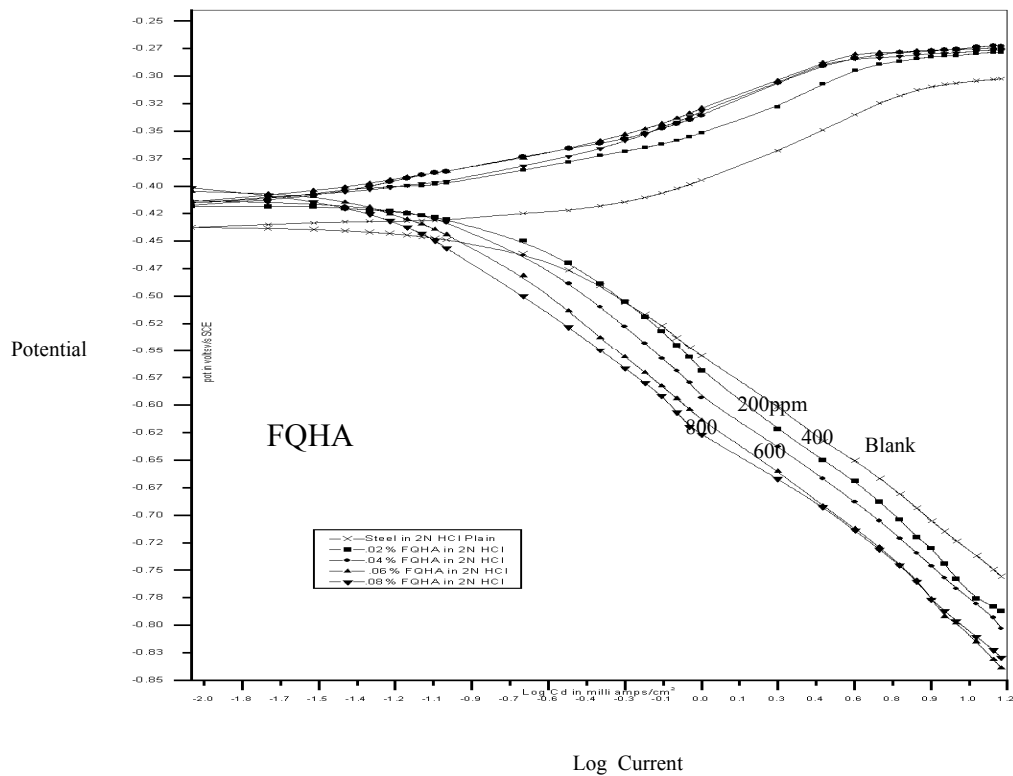


**Fig. 2.** Polarization profile of FQ in 2N HCl medium

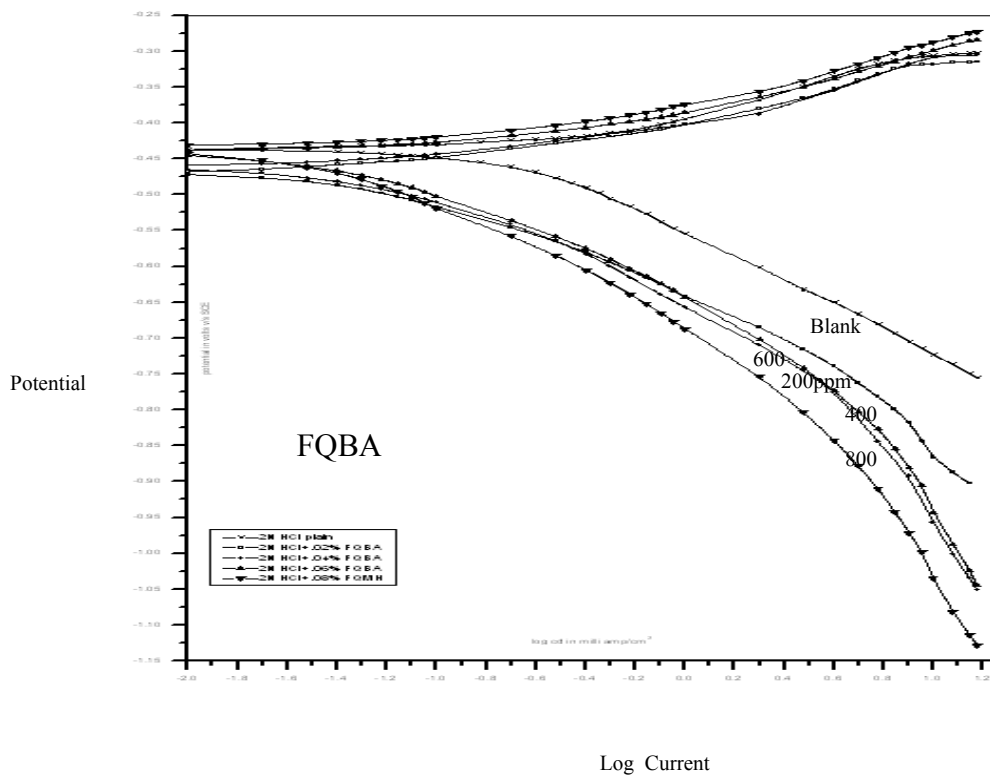


**Fig. 3.** Polarization profile of FQMh in 2N HCl medium





**Fig. 4.** Polarization profile of FQHA in 2N HCl medium



**Fig. 5.** Polarization profile of FQBA in 2N HCl medium

**Table 3.** Corrosion parameters generated by polarization method

Inhibitor	Concentration ppm	$E_{\text{corr}}$ (mV) -ve	$i_{\text{corr}}$ ( $\mu\text{Acm}^{-2}$ )	$\theta$	%IE	$b_a$ mV	$b_c$ mV
FQ	Blank	446	177.75	-	-	63	114
	200	400	70.8	0.60	60	70	167
	400	402	63.09	0.64	64	69	181
	600	405	56.2	0.68	68	75	171
	800	408	50.1	72	72	81	161
FQMH	Blank	446	177.75	-	-	63	114
	200	467	95.4	0.46	46	71	143
	400	458	79.43	0.55	55	77	149
	600	455	70.0	0.61	61	75	133
	800	452	55	0.64	69	56	117
FQHA	Blank	446	177.75	-	-	63	114
	200	422	131.8	0.26	26	83	128
	400	405	77.6	0.56	56	59	146
	600	410	75	0.58	58	65	145
	800	412	70.7	0.60	60	72	153
FQBA	Blank	446	177.75	-	-	63	114
	200	470	114.8	0.35	35	68	158
	400	475	83.1	0.53	53	53	178
	600	435	79.43	0.55	55	68	168
	800	450	65	0.63	63	79	192

### 3.4. Elevated Temperature studies

To know the performance of the inhibitor molecule at elevated temperature polarisation studies were carried out on steel coupon in 2N HCl media in the absence as well as in the presence of the inhibitors at identical concentration over three different temperatures. The enthalpy of the overall inhibition process and parameters interpreted through adsorption isotherms are tabulated in the Table 4.

**Table 4.** Thermodynamic parameters obtained by elevated temperature studies

Compound	Concentration ppm	Interaction Parameter f	Free energy change $\Delta G$ KJ/mol	Enthalpy change $\Delta H$ KJ/mole	Entropy change $\Delta S$ J/mol	Adsorption type
FQ	200	3.54	-31.31	-76.98	-150.72	Tempkin
FQMH	200	41.46	-99.78	-49.55	-165.77	Tempkin
FQHA	800	1.565	-35.71	-49.21	-44.55	Tempkin
FQBA	200	40	-70.23	-130.86	-200	Tempkin

It was found that the efficiencies of the compounds decrease with the increase in temperature. Using standard Gibbs Helmholtz equation, viz,  $-\Delta G = \Delta H - T\Delta S$ , the entropy change that occurs during the adsorption process was calculated using  $\Delta H$  and  $\Delta G$  values. The latter value was calculated from the equation  $\Delta G = RT \ln 55.5K$ , where K stands for the equilibrium constant for the adsorption and desorption reaction .

It can be seen from the results that the adsorption process proceeds with liberation of heat while the free energy change during the process of adsorption is sufficiently negative to promote hinder less deposition. The entropy parameter will normally be negative as the adsorbing species changes its phase from liquid to solid at the surface of deposition. The nature of the deposit on the surface quite oftenly decides the sign of the entropy factor. A random deposit will result in not much loss in entropy while an orderly deposit would certainly decrease entropy. The randomness or orderly ness would in all likely hoods depend on the stereochemistry of the adsorbing molecule and intermolecular cohesive factor.

The effectiveness of the as an inhibitor depends on the structure of the organic compound. The adsorption of the compounds on the metal surface occurs through interaction between

- a) The non bonding electron pair presents on the adsorbing moiety will coordinate with the electron deficient sites on the metal substrate.
- b) The loosely held delocalised  $\pi$  electrons across sites of conjugation and aromatic and heterocyclic rings bond with the positive sites on the metal substrate.

The hindrance free adsorption of the molecules on the substrate is guided by molecular geometry and symmetric factors. Any factors that affect electron density of the kind addressed above would seriously reflect in the practical inhibitory performances of the compounds.

The chances of electrons responsible for aromaticity forming coordination bonds will not arise, as it would destabilize the compound.

#### **4. CONCLUSIONS**

The inhibitors investigated decreased the corrosion rate significantly in 2N HCl media. The solubility enhancement of the inhibitors in corroding media required prior dissolution of the compounds in polar solvent mixture. The inhibitive efficiencies decrease with the increase in temperature. The inhibitory performances of the compounds against corrosion followed the order FQ>FQMH>FQBA>FQHA.

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