INHIBITION OF ACIDIC CORROSION OF LOW CARBON STEEL BY SYMMETRICAL 1,3,4-OXADIAZOLES

P. SOUNTHARI[1], A. KIRUTHIKA[2], S. CHITRA[3] & K. PARAMESWARI[4]

[1,2]Research Scholar, Department of Chemistry, P. S. G. R. Krishnammal College for Women, Peelamedu, Coimbatore, Tamil Nadu, India

[3,4]Associate Professor, Department of Chemistry, P. S. G. R. Krishnammal College for Women, Peelamedu, Coimbatore, Tamil Nadu, India

ABSTRACT

The inhibitive effect of symmetrical 1,3,4-oxadiazoles on the corrosion of mild steel in 1M H_2SO_4 was investigated by weight loss method, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy. The results showed that inhibition efficiency increases with increase in concentration of the inhibitors. The potentiodynamic polarization curves revealed that the oxadiazoles act as mixed type inhibitors. EIS measurements show an increase in charge transfer resistance with the inhibitor concentrations. The temperature effect on the corrosion behaviour of the steel in 1M H_2SO_4 with and without the inhibitor was studied in the temperature range (303-333K). The thermodynamic parameter ΔG^0 and kinetic parameter E_a have also been calculated. The inhibition efficiency has been synergistically enhanced by the addition of halide ions. The percentage of iron in the corrodent solution was determined by atomic absorption spectroscopy. The surface morphology of the mild steel specimens were evaluated using SEM images.

KEYWORDS: Adsorption, Impedance, Polarization, 1,3,4-Oxadiazole inhibitors

INTRODUCTION

The study of corrosion processes and their inhibition by organic compounds is a very active field of research [1].The effectiveness of organic compounds containing heteroatoms as corrosion inhibitors for mild steel in sulphuric acid is well developed.The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorous and sulphur, triple bonds or aromatic rings. The nature of heteroatom and substituents play a major role in the adsorption phenomenon. Also the existing data show that most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier film [2-6].Recently many workers have reoriented their attention to the development of new corrosion inhibitors based on organic compounds such as pyrazoles,triazoles, tetrazoles, imidazoles[7-9],containing heteroatoms and multiple bonds in the molecules that facilitate adsorption on the metal surface. Free electron pairs on the heteroatoms or π electrons are readily available for sharing to form a bond and also induce greater adsorption of the inhibitor molecules on to the surface of mild steel,leading to the formation of a corrosion protecting film.

The present investigation deals with the corrosion of mild steel in 1M sulphuric acid and the inhibitive effect of some symmetrical oxadiazoles derived from carboxylic acids, hydrazine hydrate and polyphosphoric acid using weight loss, gasometric method, potentiodynamic polarization and AC-impedance techniques. The influence of temperature (303K-333K) and synergistic effects by the addition of halide ions (Cl⁻, Br⁻ and I⁻) have been studied. The surface morphology of the mild steel plates in the presence and absence of the inhibitors have been examined by the analysis of the SEM photographs.

EXPERIMENTAL METHOD

Cold Rolled mild steel specimen of size 1cmx3cmx0.1cm having composition 0.084% C, 0.369% Mn, 0.129% Si, 0.025% P, 0.027% S, 0.022% Cr, 0.011% Mo, 0.013% Ni and the reminder iron were used for weight loss and gasometric measurements. For electrochemical methods, a mild steel rod of same composition with an exposed area of 0.785 cm^2 was used. The specimens were polished with 1/0, 2/0, 3/0 and 4/0 grades of emery sheets and degreased with trichloroethylene and dried using a drier. The plates were kept in a desiccator to avoid the absorption of moisture.

Synthesis of Symmetrical Oxadiazoles

The inhibitors were synthesized in one step by the reported procedure [10].

Poly phosphoric acid (40g) was taken in a round bottom flask. To this 10ml of hydrazine hydrate was added in drops, for 15 minutes with stirring, while maintaining the flask on ice water bath. To this mixture 10g of carboxylic acid was added and refluxed for 6-8 hours at 130^{0}C and then cooled at 70^{0}C.The mixture was poured with stirring to ice. The precipitate obtained was filtered and washed with sodium carbonate in order to remove excess polyphosphoric acid. The oxadiazoles were recrystallized from ethanol. The oxadiazoles were characterized by IR spectra [Figure 1].The absorption bands at (1627cm^{-1}) and (1234cm^{-1}) are assigned to (>C=N) and (=N-N=C) functional groups. Whereas absorption bands at (1057cm^{-1}) is characteristic of(-C-O-C-) stretching.

The structures of the oxadiazoles are presented in Table 1.
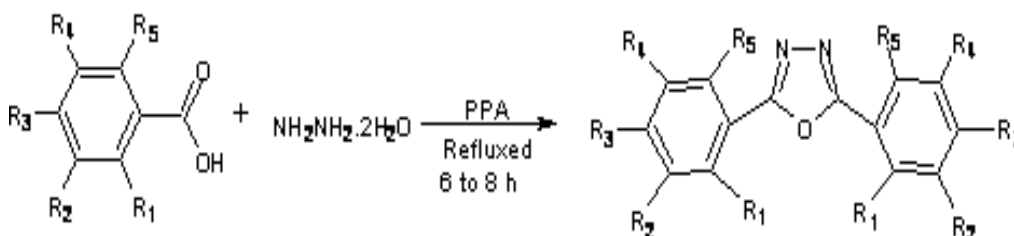
Name	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$
DPO	H	H	H	H	H
HDPO	H	H	OH	H	H
ADPO	NH$_2$	H	H	H	H
NDPO	H	NO$_2$	H	NO$_2$	H
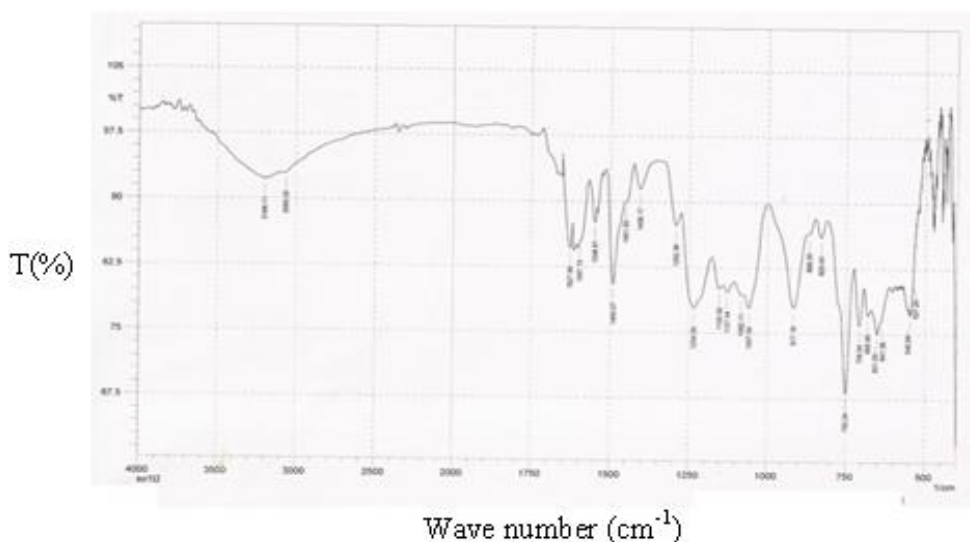
Figure 1: IR Spectrum of HDPO
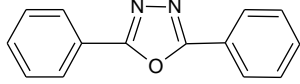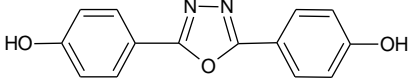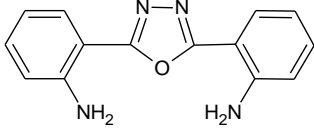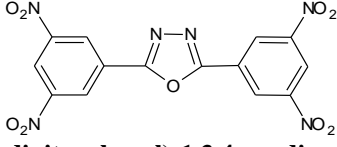
Table 1: Structure of the Symmetrical Oxadiazoles

S. No.	Structure of the Compounds	Colour	Yield (%)
1.	2,5-diphenyl-1,3,4-oxadiazole[DPO]	White	70
2.	2,5-bis(3-hydroxyphenyl)-1,3,4-oxadiazole[HDPO]	white	89
3.	2,5-bis(2-aminophenyl)-1,3,4-oxadiazole [ADPO]	Dirty yellow	90
4.	2,5-bis(3,5-dinitrophenyl)-1,3,4-oxadiazole [NDPO]	Dark biscuit	75

The corrosion resistant properties of the symmetrical oxadiazoles were investigated by various techniques.

Non-Electrochemical Techniques

Weight Loss Method

The initial weight of the polished plates was taken. The solutions were taken in 100 ml beakers and the specimens were suspended in triplicates into the solution using glass hooks. Care was taken to ensure the complete immersion of the specimen. After a period of 3 hours the specimens were removed, washed with distilled water, dried and weighed using chemical balance. From the initial and final masses of the specimen (i.e., before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various inhibitor concentrations in 1M H_2SO_4. A blank was carried out without inhibitor. The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using the formulas,

$$\text{Inhibition efficiency (\%)} = \frac{\text{Weight loss without inhibitor - Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \times 100$$

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weight loss in mgms}}{\text{Density} \times \text{Area in sq. inch} \times \text{Time in hours}}$$

$$\text{Surface coverage}(\theta) = \frac{(\text{Weight loss without inhibitor - Weight loss with inhibitor})}{\text{Weight loss without inhibitor}}$$

To study the effect of temperature, the above procedure was carried out at different temperature range i.e., (313-333K) using thermostat with the inhibitor concentration of 10mM.

Activation energy (E_a), Free energy of adsorption (ΔG^0), Enthalpy and Entropy(ΔH^0 & ΔS^0) were calculated using the formula,

- **E_a = - 2.303x8.314xslope (kJ)**
- **$K = \frac{1}{55.5}\exp\left[-\frac{\Delta G°ads}{RT}\right]$**

$$K = \frac{\theta}{C(1-\theta)} \text{[from Langmuir equation]}$$

Ɵ - Surface coverage of the inhibitor, C- concentration of inhibitor in mM/100ml

- $$CR = \left[\frac{RT}{Nh}\right] \exp\left[\frac{\Delta S^{\circ}}{R}\right] \exp\left[\frac{\Delta H^{\circ}}{RT}\right]$$

h-Plancks constant, N-Avogadro number, T-Absolute temperature, R-Universal gas constant

Gasometry

Mild steel specimen of size 1cm x3cm x0.1cm were given fine mechanical polishing and degreased with trichloroethylene. The specimens were stored in a desiccator. The net area exposed was $0.35cm^2$ approximately. The specimen was suspended from a hook on a glass stopper and introduced into the gasometric cell containing 100ml of the acid. The temperature was maintained constant throughout the experiments at $303\pm1K$ and at constant atmospheric pressure. Gas measurements were made for a period of an hour in all the cases. Simultaneously a duplicate was also performed in all the cases to check the results. Experiments were repeated under identical conditions for inhibitor solutions of different concentration and the gas volume was measured for duration of an hour. From the volume of hydrogen gas liberated the inhibition efficiency was calculated using the formula

$$I.E(\%) = \frac{(V_B - V_I)}{V_B} X\ 100$$

V_B and V_I= the volume of hydrogen evolved in the absence and presence of inhibitor.

Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectrophotometer (Model GBC 908, Australia) was used for estimating the amount of dissolved iron in the corrodent solution containing various concentrations of DPO and HDPO in 1M H_2SO_4 after exposing the mild steel specimen for 3hours. From the amount of dissolved iron, the inhibitor efficiency was calculated.

$$I.E(\%) = \frac{(B-A)}{B} x\ 100$$

Where, **A** and **B** = Amount of dissolved iron in the presence and absence of inhibitors

Electrochemical Techniques

The electrochemical measurements were performed in a classical three-electrode cell assembly with mild steel rod (exposed area $0.78\ cm^2$) as working electrode, a platinum electrode and saturated calomel electrode as counter and reference electrodes.

The measurements were carried out with IVIUM Compact stat Potentiostat/Galvanostat. EIS measurements were carried out at a frequency range of 10KHz to 0.01Hz with a superimposed sine wave of amplitude 10mV. From the plot of Z^1 Vs Z^{11} the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated.

$$I.E(\%) = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} X\ 100$$

Where, R_{ct} and R_{ct}^* are the charge transfer resistance obtained in the absence and presence of the inhibitors.

The potentiodynamic polarization curves were obtained from -200mV to +200mV (versus OCP) with a scan rate of 1 mV/s. The data were collected and analyzed by IVIUM Soft software.

$$I.E\,(\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

Where, I_{corr} and $I_{corr(inh)}$ signifies the corrosion current density in the absence and presence of inhibitors.

Synergism

The synergistic effect was studied by the addition of 1mM KCl / KBr / KI to the mild steel specimen immersed in 1M H_2SO_4 containing various concentrations of the inhibitors for duration of three hours. From the weight loss the inhibition efficiency was calculated.

Surface Morphology

Surface examinations of mild steel specimens were carried out to understand the surface morphology of mild steel in 1M H_2SO_4 in the presence and absence of the inhibitors (Blank, HDPO, ADPO) using Medzer biomedical research microscope (Mumbai, India).

RESULTS AND DISCUSSIONS

Weight Loss Measurements, Adsorption Isotherms and Thermodynamic Parameters

Inhibitor efficiency(%) obtained from weight loss measurements for different concentrations of DPO, HDPO, ADPO and NDPO in 1M H_2SO_4 are given in (Table.2) and the results are depicted in (Figure 2).

Table 2: Inhibition Efficiencies of Various Concentrations of the Inhibitors for Corrosion of Mild Steel in 1M H_2SO_4 Obtained by Weight Loss Measurement at 30 ± 1^0C

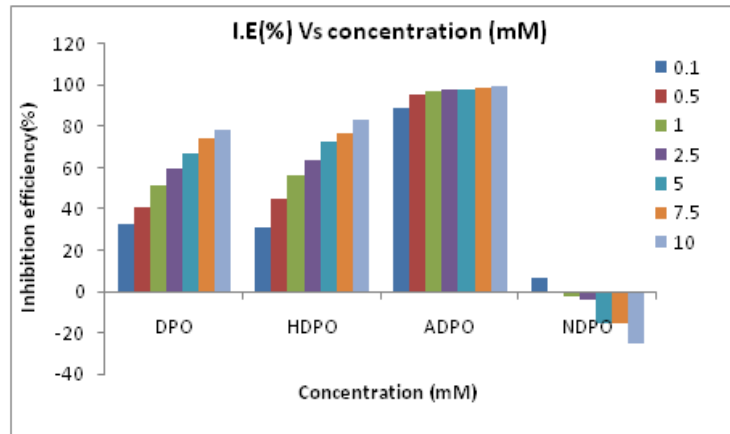| Name of the Inhibitors	Concentra-tion (mM)	Weight Loss (g)	Inhibition Efficiency (%)	Degree of Surface Coverage(Θ)	Corrosion Rate (mpy)
	Blank	0.2209	-	-	-
DPO	0.1	0.1486	32.7	0.3272	62330.06
	0.5	0.1192	46.0	0.4603	49998.27
	1	0.1062	51.6	0.5192	44545.44
	2.5	0.0900	59.2	0.5925	37750.37
	5	0.0736	66.7	0.6668	30871.41
	7.5	0.0569	74.2	0.7424	23866.62
	10	0.0475	78.5	0.7849	19923.80
HDPO	0.1	0.1518	31.3	0.3132	63654.15
	0.5	0.1224	44.6	0.4457	51331.01
	1	0.0963	56.4	0.5643	40397.69
	2.5	0.0799	63.8	0.6386	33541.2
	5	0.0612	72.3	0.7231	25665.5
	7.5	0.0506	77.1	0.7710	21218.05
	10	0.0367	83.4	0.8340	15380.77
ADPO	0.1	0.0251	88.6	0.8863	10528.15
	0.5	0.0120	95.5	0.9456	5033.38
	1	0.0060	97.2	0.9728	2516.69
	2.5	0.0046	97.9	0.9791	1929.46
	5	0.0041	98.1	0.9814	1719.73
	7.5	0.0035	98.5	0.9841	1468.07
	10	0.0011	99.5	0.9950	461.39
NDPO	0.1	0.0260	6.7	0.06745	86406.40
	0.5	0.2216	-0.3	-0.00316	92949.80
	1	0.2265	-2.5	-0.0253	95005.10
	2.5	0.2306	-4.4	-0.0439	96724.84
	5	0.2545	-15.2	-0.1521	106749.66
	7.5	0.2547	-15.3	-0.1530	106833.55
	10	0.2767	-25.3	-0.2526	116061.42

Figure 2: Plot of Inhibition Efficiency (%) Vs Concentration (mM) for the Inhibition of Corrosion of Mild Steel in 1M H$_2$SO$_4$

The data reveals that the oxadiazoles DPO, HDPO and ADPO are moderate to excellent inhibitors for corrosion of mild steel in acid medium. The inhibition efficiency increased with increase in the concentration of the oxadiazoles but decreased with temperature (Table.3) which suggests that the corrosion inhibition of the oxadiazoles for mild steel might be caused by the adsorption of the inhibitors onto the steel surface from acidic solution while higher temperatures might cause the desorption of the inhibitors from the steel surface. The inhibitor ADPO exhibited an efficiency of 99% at a concentration of 10mM.The order of inhibition efficiency is ADPO>HDPO>DPO>NDPO.

Basic information on the interaction between the inhibitor molecules and the metal surfaces can be provided from adsorption isotherms. A correlation between surface coverage Ө and the inhibitor concentration in the corrosive medium can be represented by the Langmuir adsorption isotherm.

Ө/(1-Ө)=k $_{ads}$ C   (1)

Where k$_{ads}$ are the equilibrium constant of the inhibitor adsorption process and 'C' is the inhibitor concentration. A plot of C/Ө Verses C yielded a straight line (Figure 3) confirming that the adsorption of the oxadiazoles on the metal surface obeyed Langmuir adsorption isotherm model.

The free energy of adsorption (ΔG^0_{ads}) was calculated from the equilibrium constant of adsorption at different temperatures using the following equation:

ΔG^0_{ads}= - RT ln (55.5k)   (2)

From (Table.4) it is evident that ΔG^0_{ads} becomes more positive with increase of temperature. This result indicated that the adsorption of the oxadiazoles on the mild steel surface was unfavourable to the experimental temperature[11]. The negative values of ΔG^0_{ads} for DPO, HDPO and ADPO confirmed the spontaneous adsorption of the inhibitors on mild steel surface. For NDPO, ΔG^0_{ads} is positive and increases with increase in temperature proving that adsorption of NDPO onto the mild steel plate has not occurred (ie) addition of NDPO has accelerated the corrosion process. Generally values of ΔG^0_{ads} upto -20kJ/mole are consistent with electrostatic interaction between charged molecule and a charged metal which indicates physisorption while those more negative than -40kJ/mole involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond which indicates chemisorption [12-14]. The values of ΔG^0_{ads} in our measurements ranged from -14.35 to -29.6kJ/moles. Thus the adsorption of the oxadiazoles DPO, ADPO and HDPO on steel in 1M H$_2$SO$_4$ must be a combination of physisorption and chemisorption in which physisorption predominates.

Table 3: Inhibition Efficiencies of 10mM Concentrations of the Inhibitors for Corrosion of Mild Steel in 1M H_2SO_4 Obtained by Weight Loss Measurement at Higher Temperature

Name of the Inhibitor	Tempe-rature (K)	Weight Loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mpy)
Blank	303	0.0736	-	30871.1
	313	0.1350	-	56625.0
	323	0.1979	-	83124.4
	333	0.2846	-	119373.8
DPO	303	0.0158	78.5	6627.2
	313	0.0484	64.2	20312.5
	323	0.0977	32.1	56410.4
	333	0.2338	17.8	98066.1
HDPO	303	0.0122	83.4	5124.39
	313	0.0758	65.7	31793.9
	323	0.1277	42.2	53638.1
	333	0.2038	7.74	85482.7
ADPO	303	0.0004	99.5	167.8
	313	0.0036	97.3	1510.0
	323	0.0152	90. 9	6390.8
	333	0.0522	81.7	21895.0
NDPO	303	0.0922	-25.3	38672.8
	313	0.1703	-26.2	71431.4
	323	0.2175	-29.5	91229.1
	333	0.3780	-32.8	158550.0
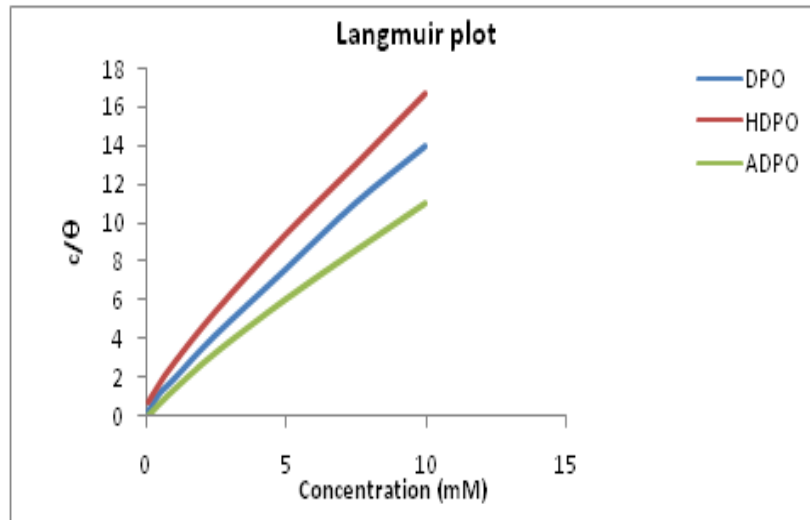
Figure 3: Langmuir Plot of Inhibitors in 1M H_2SO_4

Table 4: Kinetics/Thermodynamic Parameters of Mild Steel Corrosion in1M H_2SO_4

Name of the Inhibitor	E_a (kJ)	ΔG^0_{ads}				ΔH^0 kJ/Mole	ΔS^0 kJ/Mole
		303 K	313 K	323K	333 K		
Blank	35.89	-	-	-	-	-	-
DPO	76.63	-23.039	-20.457	-14.355	-24.604	-12.1822	-0.6407
HDPO	84.99	-24.705	-22.146	-18.146	-27.214	-19.7429	-0.8366
ADPO	135.15	-25.210	-22.878	-22.236	-29.060	-71.5907	-0.2426
NDPO	37.58	24.933	23.601	25.337	29.405	31.6476	1.3129

The activation energy E_a was calculated from the slope obtained by plotting log corrosion rate Vs 1000/T (Figure 4, Table.4) E_a in the presence of the oxadiazoles are higher than those in the uninhibited acid solution (35.89kJ/mole). This indicates physical adsorption mechanism [15,16].
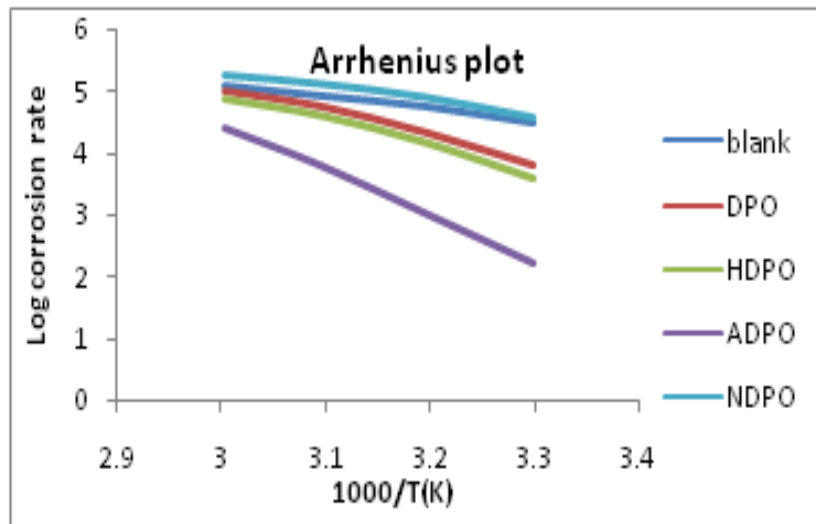
Figure 4: Arrhenius Plot of Corrosion of Mild Steel in 1M H$_2$SO$_4$ Solution in the Absence and Presence of Inhibitors

The negative values of ΔH^0 (Table.4) also show that the adsorption of the inhibitor is an exothermic process [17] which indicates that the inhibition efficiency decreases with increasing temperature. Generally an exothermic process signifies either physisorption or chemisorption while endothermic process is attributable unequivocally to chemisorptions[18].

In an exothermic process, physisorption is distinguished from chemisorption from ΔH^0 value which would be lower than 41 kJ/mole while ΔH^0 value for a chemisorption process approaches 100kJ/moles [19]. In the present case ΔH^0 values range from -12.18 to -71.59kJ/mole proving that a comprehensive adsorption (physical and chemical adsorption) might occur.

The negative values of ΔS^0 (Table.4) can be explained in the following way: before the adsorption of inhibitors onto the metal surface, inhibitor molecules freely move in the bulk solution (the inhibitor molecules are chaotic), but with the progress in the adsorption, inhibitor molecules are orderly adsorbed onto the steel surface, as a result a decrease in entropy results[20].

Electrochemical Measurements

Polarization Curves

Polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. Polarisation curves of mild steel in 1M H$_2$SO$_4$ solutions without and with different concentrations of ADPO are shown in (Figure 5).

The anodic and cathodic current potential curves are extrapolated upto their interaction at a point where corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are obtained [21]. (Table .5) shows the electrochemical parameters Icorr, Ecorr, ba and bc obtained from Tafel plots. From (Table.5) it is evident that increasing the concentration of the Oxadiazoles reduces both the cathodic and anodic currents and there is no definite trend in the shift of E_{corr} values.

The Tafel constants b_a and b_c are both affected by the addition of inhibitors but b_c to a slightly greater extent. Based on this observation it can be concluded that the inhibitors are of mixed type (ie) they reduce anodic dissolution and also retard cathodic hydrogen evolution reaction. An exception to the above result is observed with the inhibitor NDPO. NDPO accelerated both cathodic and anodic reactions and consequently stimulated corrosion as concentration is increased (% I.E = - 47.3).

Table 5: Corrosion Parameters for Corrosion of Mild Steel with Selected Concentrations of the Inhibitors in 1M H_2SO_4 by Potentiodynamic Polarization Method

| Name of the Inhibitor	Concen-tration (mM)	Tafel Slopes (mV/dec)		E_{corr} (mV)	I_{corr} ($\mu Amp/cm^2$)	Inhibition Efficiency (%)
		b_a	b_c			
Blank	-	66	96	-523.6	328	-
DPO	0.1	55	150	-475.1	213.7	34.8
	5.0	49	142	-475.8	194.5	40.7
	10.0	45	160	-473.1	177.2	45.6
HDPO	0.1	44	137	-471.1	201.4	38.6
	5.0	29	198	-441	123.3	62.4
	10.0	49	184	-469.7	88	73.2
ADPO	0.1	42	148	-466.4	142.6	56.5
	5.0	28	173	-450.8	116.2	64.6
	10.0	29	177	-443.1	102.2	68.6
NDPO	0.1	65	130	-488.7	208.8	36.3
	5.0	47	140	-473.0	288.4	12.1
	10.0	78	179	-460.5	483.2	-47.3
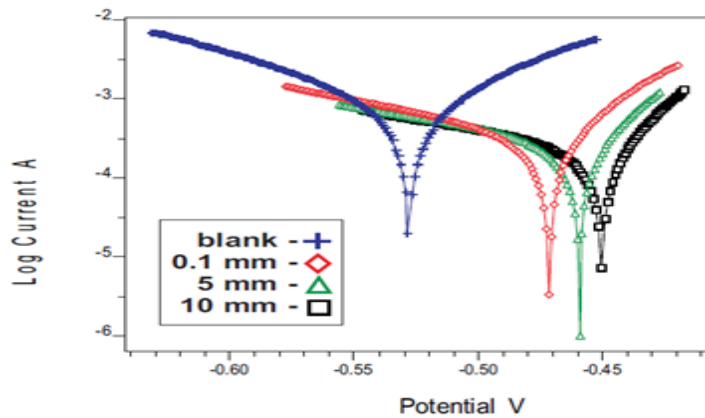
Figure 5: Polarization Curves for Mild Steel Recorded in 1M H_2SO_4 of Selected Concentrations of the Inhibitor ADPO)

Electrochemical Impedance Spectroscopy

The corrosion behavior of mild steel in acidic solution in the presence of oxadiazoles was investigated by EIS at 30 ± 1^0C. Nyquist plots of mild steel in uninhibited and inhibited acidic solutions containing various concentrations of ADPO displayed one capacitive arc (Figure 6). The impedance parameters derived from the Figures are given in the (Table.6).

Table 6: AC-Impedance Parameters for Corrosion of Mild Steel for Selected Concentrations of the Inhibitors in 1M H_2SO_4

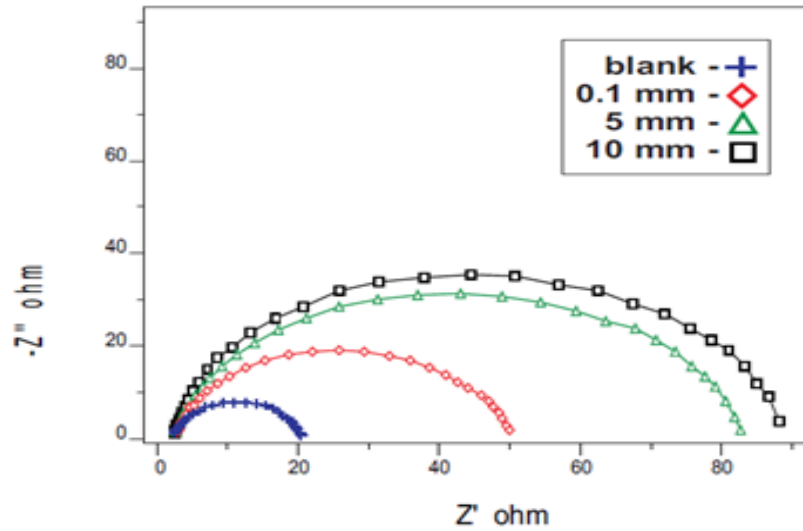| Name of the Inhibitor	Concentra-tion (mM)	R_t (ohm cm^2)	$C_{dl}(\mu F/cm^2)$	Inhibition Efficiency (%)
Blank	-	13.61	36.8	-
DPO	0.1	36.78	32.8	63.0
	5.0	37.24	27.7	63.4
	10.0	45.12	26.2	69.8
HDPO	0.1	18.65	28.7	27.0
	5.0	30.13	21.2	54.8
	10.0	36..8	18.8	63.0
ADPO	0.1	38.46	22.6	64.6
	5.0	67.01	23.2	79.7
	10.0	74.14	24.2	81.6
NDPO	0.1	17.16	40.8	20.68
	5.0	12.28	38.6	-10.8
	10.0	11.3	37.6	-20.4

Figure 6: Nyquist Diagram for Mild Steel in 1M H_2SO_4 for Selected Concentrations of Inhibitor (ADPO)

From the (Table.6) it is clear that as concentration of the inhibitor increases charge transfer resistance R_{ct} increases (except NDPO) and double layer capacitance C_{dl} decreases. For NDPO R_{ct} decreases with increases in concentration and C_{dl} values are higher compared to the blank. The inhibitor NDPO stimulates corrosion.

The acceleration by NDPO may be attributed to the following factors: (i) the lowering of overpotential for the cathodic process (ii) stimulation through preferential paths of partial electrochemical reactions in corrosion process (iii) stimulation caused by inhibitor participation in the metal dissolution process [22].

According to Donahue et al., the acceleration of corrosion in the presence of organic compounds is related to the oxidative propensity of the surface chelates.

It takes place until the chelate is adsorbed. If charge transfer comes about with the desorption of the complex ion, according to the reaction the additive will undoubtedly act as stimulator [23].

$$[(FeOH).\ inh_n]_{ads} = [(FeOH).\ inh_n]^+_{sol} + e^- \tag{3}$$

Synergism

The synergistic effect provided by the addition of halide ions I^- , Br^- and Cl^- to the solutions containing 1M H_2SO_4 and the oxadiazoles was studied by weight loss method and the data are presented in (Table.7) . Analysis of the data reveals that the synergistic influence of halide ions follows the order

$I^- > Br^- > Cl^-$
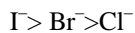
The highest synergistic influence exhibited by iodide ion may be explained as follows.

The steel surface is originally positively charged in 1M H_2SO_4 .when I^- is added to the inhibiting solution they are strongly chemisorbed by forming chemical bonds even leading to the formation of iron halide[24].

This strong chemisorption of I^- ions shift Φ_n of the metal to more positive potential than Cl^- and Br^- and renders the surface highly negatively charged.

On the highly negatively charged metal surface the protonated cationic inhibitor molecules are physisorbed due to electrostatic interaction. This interaction is higher for I^- than for Cl^- or Br^- due to higher magnitude of negative charge on the metal surface. Hence the observed order $I^- > Br^- > Cl^-$.

Significance of Synergism Parameter

The synergism parameter 'S' is defined by the relation

$$S = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

$$I' = I_1 + I_2$$

Where I_{1+2} is the measured inhibitor efficiency of the anions plus organic cations, I_1 and I_2 is the inhibitor efficiency of anions (halides) and of cations (inhibitors) (Table.7).

Table 7: Synergistic Effect of 1mM KCl / KBr / KI on the Inhibition
Efficiency of Inhibitors by Weight Loss Method at 30±1°C

Name of the Inhibitor	Concentra-tion (mM)	Inhibition Efficiency (%)				Synergistic Parameters		
		without KCl, KBr and KI	with 1mM KCl	with 1mM KBr	with 1mM KI	with 1mM KCl	with 1mM KBr	with 1mM KI
DPO	0.25	19.4	20.6	36.9	45.2	1.2	1.05	1.2
	0.50	32.7	32.9	38.1	48.4	1.04	1.09	1.5
	0.75	43.2	39.8	45.2	56.2	1.08	1.1	1.7
	1.00	47.6	43.6	51.9	59.9	1.07	1.09	1.4
	1.50	484	48.2	55.6	62.1	1.0	1.08	1.2
	3.0	55.3	57.3	58.2	66.0	1.01	1.05	1.3
HDPO	0.25	43.4	67.6	80.5	88.0	1.09	1.1	1.2
	0.50	48.3	85.2	87.9	93.3	1.05	1.02	1.18
	0.75	63.3	87.3	91.7	95.8	1.04	1.8	1.26
	1.00	77.8	88.7	93.5	96.8	1.08	1.2	1.35
	1.50	80.7	93.6	94.6	98.6	1.0	1.4	1.38
	3.0	84.1	96.3	97.0	99.5	1.02	1.42	1.4
ADPO	0.25	66.5	66.8	96.0	97.4	1.08	1.2	1.68
	0.50	81.3	85.3	96.8	98.1	1.04	1.25	1.2
	0.75	86.5	86.8	97.5	98.2	1.06	1.27	1.3
	1.00	86.7	90.0	97.7	98.3	1.09	1.29	1.46
	1.50	90.6	92.6	98.0	98.5	1.12	1.35	1.6
	3.0	93.8	94.5	98.3	98.6	1.24	1.38	1.8
NDPO	0.25	8.0	2.1	13.4	28.0	1.2	1.5	1.6
	0.50	4.0	2.5	15.8	33.7	1.3	1.9	1.7
	0.75	3.7	3.0	15.9	36.1	1.4	1.7	1.8
	1.00	2.6	3.1	17.6	38.3	1.8	1.9	1.2
	1.50	2.3	8.3	23.8	40.0	1.4	1.5	1.6
	3.0	-3.2	20.6	24.8	43.3	1.8	1.4	1.9

The significance of synergism parameter 'S' is that a value of S>1 denotes synergism while a value of S<1 denotes antagonism. The synergism parameter calculated for the three halide ions is presented in (Table.7). The 'S' values are greater than unity indicating that the corrosion inhibition by the oxadiazoles has been enhanced by the addition of halide ions which have synergistically influenced the inhibition.

Further the 'S' value increases in the order $Cl^- <$ $Br^- <$ I^- giving highest synergistic influence for I^- which is in accordance with the findings noted in literature[25].

Atomic Absorption Spectrophotometric Studies (AAS)

The inhibitor efficiency (%) of the oxadiazoles HDPO and ADPO was calculated from the percentage of Fe dissolved, obtained from AAS and the data are presented in (Table.8). The inhibitor efficiency (%) obtained by this technique was found to be in good agreement with that obtained from the conventional weight loss method.

**Table 8: Amount of Dissolved Iron Present in the Corrosive Solution with and without
Inhibitors in 1M H_2SO_4 Measured Using Atomic Absorption Spectroscopy**

Name of the Inhibitor	Concentra-tion (mM)	Amount of Iron Content (mg/l)	Inhibition Efficiency (%)
HDPO	Blank	1304.96	-
	0.1	949.42	27.24
	10	203.98	84.38
ADPO	0.1	192.82	85.22
	10	58.63	95.50

Surface Morphology

The mild steel specimens immersed in the blank acid (1M H_2SO_4) and inhibited acid (1M H_2SO_4 + 10mM of ADPO) were observed under a scanning electron microscope and the photographs are shown in (Figure 7 and 8). The photographs show that the mild steel was heavily corroded in 1M H_2SO_4 (Figure 7) where as in the presence of inhibitor the surface condition was comparatively better (Figure 8). This suggests the presence of protective adsorbed layer of inhibitor molecules on the mild steel surface which indicates the corrosion rate of the metal appreciably.

Figure 7 (Blank)   Figure 8 (HDPO)
Figure 7&8: Scanning Electron Microscopy Photographs in the Absence and Presence of Inhibitors
Mechanism of Inhibition

It is well known that the presence of an organic molecule in the acid medium inhibits corrosion of metals by adsorbing at the metal- solution interface. The modes of adsorption are dependent on (i) the chemical structure of the molecule (ii) the chemical composition of the solution (iii) the nature of the metal surface and (iv) the electrochemical potential of the metal solution interface [26].The most important aspect of inhibition normally considered by corrosion scientist is the relation between the molecular structure and corrosion inhibition efficiency.

In the present work the oxadiazoles are expected to get adsorbed on the mild steel surface in three ways

- In acidic solution the compounds can exist as protonated species. The probable site of protonation being the nitrogen atom of the oxadiazole ring. These protonated species may adsorb on the cathodic sites of mild steel and decrease hydrogen evolution.

- These compounds may get adsorbed on anodic sites through lone pair of electrons on the nitrogen, oxygen atoms and π -electrons of the aromatic rings, which decreases the anodic dissolution of mild steel.

- Combination of the above two [27] (Figure 9)

All the oxadiazoles have almost the same size but they possess different substituent groups. The best performance of ADPO and HDPO (I.E% =99.5 and 83.4% at 10 mM) may be attributed to the presence of electron releasing -NH_2 and – OH groups respectively which increases the π- electron density on the phenyl ring. In the case of NDPO the inhibition efficiency values are negative, which may be attributed to the presence of four electron withdrawing –NO_2 groups. This

decreases the π- electron densities on the aromatic rings which decreases the adsorption process and hence stimulate corrosion.

The IR spectrum of the plate immersed in the 1M H_2SO_4 containing 10mM DPO (Figure 10) shows a sharp peak around $1740cm^{-1}$. A review of literature reveals that substituted oxadiazole are sensitive to acids and they get readily hydrolyzed at room temperature to benzhydrazide and benzoic acid. In addition they also undergo ring opening reaction on treatment with acids [28]. Based on the above, it can be concluded that the oxadiazoles under study has probably dissociated to benzhydrazide and benzoic acid. These dissociation products have got adsorbed onto the mild steel surface inhibiting the corrosion process. As evidenced by the peak in the IR spectrum at $1740cm^{-1}$is characteristic of products of decomposition of DPO.
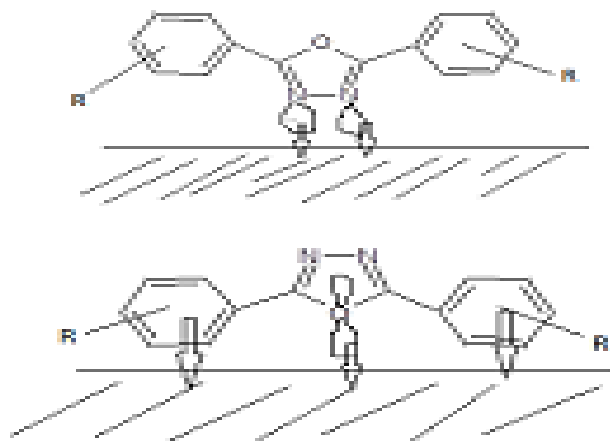

Figure 9: Schematic Diagram of Adsorption of Oxadiazoles of Mild Steel Surface
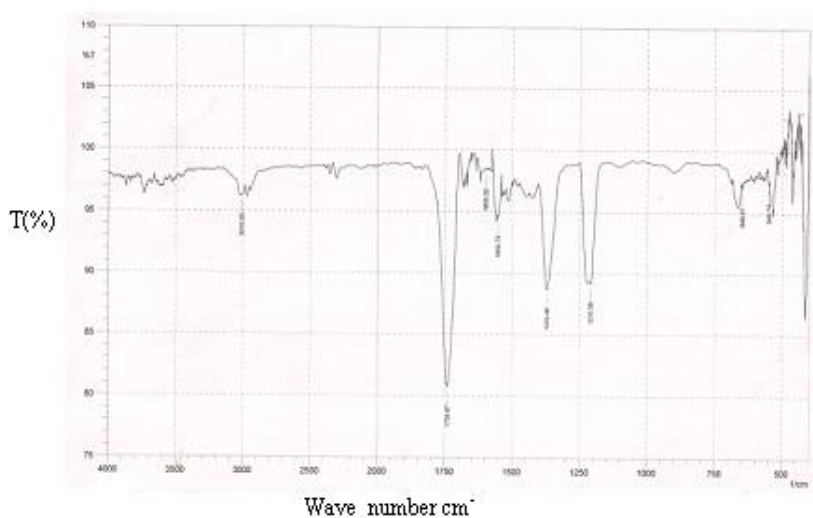

Figure 10: IR Spectrum of DPO

Computational Studies

The optimized geometry of the polymers along with HOMO, LUMO and electron density map are derived from Arguslab software. Figure 11 shows the optimized geometry of DPO. The corresponding parameters are given in Table-9.

Table 9: Parameters Derived from Computational Studies

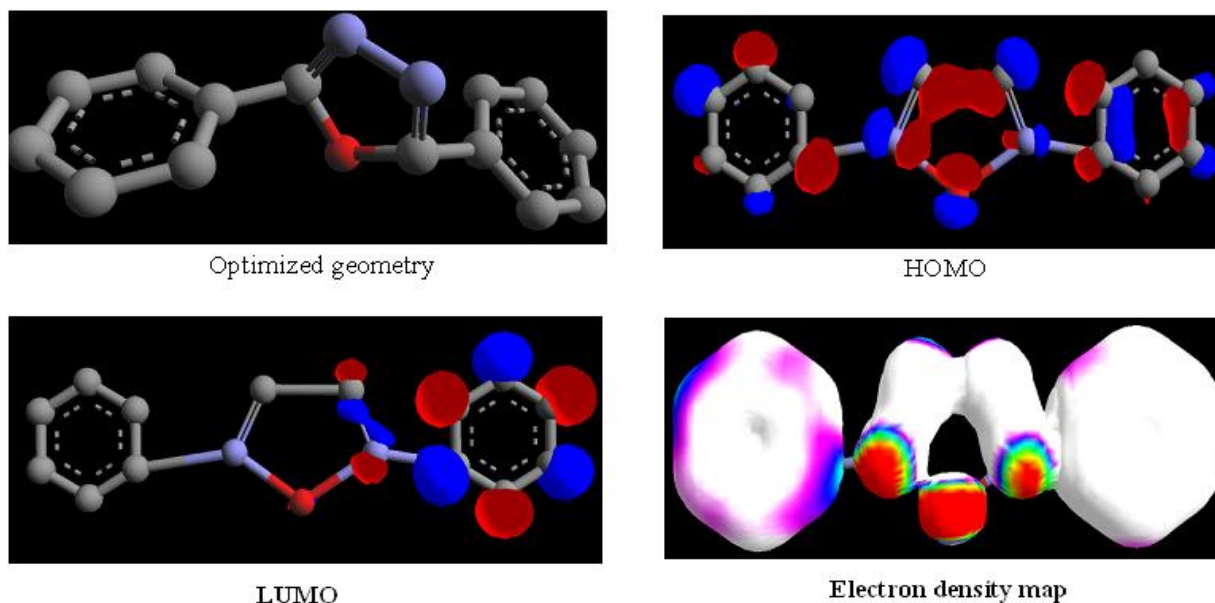| Name of the Inihibitors	Core Repulsion (au)	Final SCF Energy (kcal/mol)	Heat of Formation (kcal/mol)
DPO	307.962	-56775.0366	1531.5704
HDPO	401.959	-71710.2407	1294.0249
ADPO	441.244	-60929.2773	8198.0110
NDPO	948.644	-127312.2642	8907.1064

Figure 11: Optimized Geometry, HOMO, LUMO and Electron Density Map of DPO

CONCLUSIONS

The Conclusions Arrived Based on the Investigations are

- The order of inhibition efficiency of the synthesized compounds are ADPO>HDPO>DPO>NDPO.

- All investigated inhibitors are effective inhibitors for corrosion of mild steel in 1M H_2SO_4 except NDPO.

- The adsorption of inhibitors on the mild steel surface obey Langmuir adsorption isotherm.

- The activation energy (E_a) is higher for inhibited acids than for uninhibited acids showing the temperature dependence of inhibition efficiency except NDPO.

- The less negative values of $\Delta G°_{ads}$ indicate the spontaneous adsorption of the inhibitors on the metal surface. For the inhibitor NDPO, ΔG^0_{ads} values are positive. This confirms that the adsorption process for NDPO is not spontaneous. This is further proved by the I.E values obtained from weight loss measurements.

- Electrochemical impedance spectroscopy experiments have shown that an increase in inhibitor concentration causes an increase in charge transfer resistance R_t and a decrease in C_{dl} value, owing to the increased thickness of the adsorbed layer.

- The Tafel slopes obtained from potentiodynamic polarization curves indicate that all the inhibitors behave as mixed type.

- Addition of halide ions to the inhibitors shows an increase in inhibition efficiency.

- The inhibition efficiency obtained from atomic absorption spectrophotometric studies was found to be in good agreement with that obtained from the conventional weight loss method.

REFERENCES

1. P. Udhayakala, T.V.Rajendiran, S.Gunasekaran, J. Adv. Sci. Res, 3(3) (2012) 67.

2. A. Jamal Abdul Nasser, Int.J.Engineering Science and Technology. 2(11) (2010) 6417.

3. M.Lagrenee,B.Mernari, N.Chaibi, M.Traisnel,H.Vezin, F.Bentiss.,Corrosion Science 44 (2002) 573.

4. R.T.Loto,C.A.Loto and A.P.I.Popoola, Int.J.Electrochem.Sci.,7(2012) 7016.

5. EnoE.Ebenso,ImeB.Obot, L.C.Murulana,Int.J.Electrochem.Sci.,5(2010)1574.

6. Ajmal M, Mideen AS, Quaraishi MA. Corros. Sci., 36(1994)79.

7. M.Benabdellah1, B.Hammouti1, A.Warthan, S.S.Al-Deyab, C.Jama, M.Lagrenée, F.Bentiss5 Int. J. Electrochem. Sci., 7 (2012) 3489.

8. Abdel – Aal, M.S.and Morad,M.S, Brit.Corros.J., 36 (2001) 253.

9. F.Bentiss, M.Outirite, M.Traisnel, H.Vezin, M.Lagrenée, B. Hammouti, S.S.Al-Deyab, C.Jama,Int J.Electrochem.Sci.,7 (2012) 1699.

10. Mariana Dana Iosip, Maria Bruma, Inga Ronova, Marta Szesztay, Peter Muller, European polymer journal 39(2003) 2011.

11. Zhihua Tao, shengtau Zhang, Weihua Li and BaorongHou, Corrosion science, 51 (2009) 2588.

12. M.A.Quarshi, R.Sardar, Mater, J.applied electrochemistry, 32(2002) 425.

13. Libin Tang, Guannan Mu, Guangheng Liu, Corrosion science, 45(2003) 2251.

14. K.Tebbji, N.Faska, A.Tounsi, Mater.Chem.Phys., 106(2007)260.

15. A.Popova, E.Sokolova, S.RaichevaandM.Christov,Corrosion science, 45(2003)33.

16. M.Benabdellsah, A.Dafali, B.Hammouti, A.Aouniti, M.Rhomari, A.Raada, O.Senhaji and J.Robin, J. Chem. Eng. Commun, 194(2007)1328.

17. M.K.Gomma, M.H.Wahdan, Mater. Chem. Phys. 39(1995)209.

18. W.Durnie, R.De Marco, B.KinsellaandA.Jefferson, J. Electrochem. Soc., 146(1999)1751.

19. S.Martinez and I.Stern, Appl. Surf. Sci.,199(2002)83.

20. K.Tebbji, A.Aouniti, A.Attayibat, B.Hammouti, H.Oudda, M.Benkaddour, S.Radi and A.Nahle, Indian. J.Chem.Tech.,18(2011)244.

21. S.S.AbdEl.Rehim, M.A.M.Ibrahim, K.F.Khaled, J.Appl. Electrchem., 29 (1999) 593.

22. A.Frignani, G.Trabanelli, F.Zuckhi, M.Zucchini, Proc.Fourth European Symposium on Corrosion inhibitors, Ann.Univ, Ferrara, N.S.Sez V, Suppl. N.6(1975)652.

23. F.M.Donahue, A.Akiyama, K.Nobe ,J. Electrochem.Soc., 114(1967)1006.

24. R.Saratha, C.Marikkannu and S.Sivakama sundari, Bull.Eletrochem., 18(2002) 141.

25. A.S.Fouda, H.A.Mostafa, F.El-Taib and G.Y.Elewady, Corrosion Sci., 47 (2005) 1988.

26. A.S.Fouda, H.A.Mostafa, F.El-Taib and G.Y.Elewady and M.A.El-Hashmey, Chem.Eng.Commun., 196(2009) 1536.

27. M.Karakus, M.Shin, S.Bilgic, Mater. Chem.Phy., 92(2005) 565.

28. Julio Alvarez-Builla,Juan J.Vaquero and Jose Barlunga,Modern Heterocyclic Chemistry, Wiley-Vclt, 13(1961) 1214.