



RESEARCH ARTICLE

OXADIAZOLE POLYAMIDES: NEW AND EFFECTIVE CORROSION INHIBITORS FOR MILD STEEL IN 1M H₂SO₄

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ABSTRACT

A series of new heterocyclic polyamides, containing symmetrical 1, 3, 4-oxadiazole rings, was synthesized by condensation of bis (4-amino phenyl)-1,3,4-oxadiazole with aliphatic and aromatic dicarboxylic acids. The efficiency of the polymers has been studied for corrosion inhibition of mild steel in 1M H₂SO₄ by weight loss, polarization technique, electrochemical impedance spectroscopy and scanning electron microscopy. The results showed that the inhibition efficiency increases with increase in concentration and decreases with increase in temperature. The inhibition efficiency has been synergistically enhanced by the addition of halide ions and the thermodynamic parameter ΔG^0 and kinetic parameter E_a have also been calculated. The adsorption of these compounds was found to obey Langmuir adsorption isotherm. The percentage of iron in the corrosive solution was determined by atomic absorption spectroscopy. The surface morphology of the mild steel specimens was evaluated using SEM images.

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INTRODUCTION

Corrosion of iron and steel in acidic aqueous solutions is one of the major areas of concern in many industries where in acids are widely used for applications such as acid pickling, acid cleaning, acid descaling and oil well acidizing. Due to the general aggressiveness of acid solution the materials of construction are getting corroded easily. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media. Most well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The inhibiting action exercised by organic compounds on the dissolution of metallic species is normally related to interactions by adsorption between the inhibitors and the metal surface (Abd *et al.*, 2011). In the past few years, polymers have been recognized as excellent corrosion inhibitors for metals in acid environment (AbdallaAbulkibash *et al.*, 2008). Polymeric compounds consist of large molecules which can be adsorbed on the surface of a certain metal, hence, polymers can be considered as corrosion inhibitors and they also play a crucial role in protecting metals against corrosion (Shokry, 2009).

A small quantity of polymer may be effective in inhibiting the corrosion of metals. Through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatoms that are the major active centers of adsorption (Umoren, 2009). The aim of the present work is to investigate the inhibitory effects of new heterocyclic polyamides, containing symmetrical 1,3,4-

oxadiazole rings, synthesized by condensation of bis(4-aminophenyl)-1,3,4-oxadiazole and aliphatic with aromatic dicarboxylic acids. The efficiency of the polymers has been studied for corrosion inhibition of mild steel in 1M H₂SO₄ by weight loss, polarization technique, electrochemical impedance spectroscopy and scanning electron microscopy. The influence of temperature (303-333K) and synergistic effects by the addition of halide ions (Cl⁻, Br⁻ & 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 1cm x 3cm x 0.1cm 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 remainder 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 cm² 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 inhibitors

Polyamides containing oxadiazole were obtained by condensation reaction of symmetrical oxadiazoles and diacid chlorides.

Synthesis of monomers

The oxadiazole monomer was synthesized by the reaction of p-amino benzoic acid with hydrazine hydrate in polyphosphoric

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acid (PPA) (Ion Sava *et al.*, 2003). The aliphatic/aromatic diacid chlorides were prepared from thionyl chloride and corresponding dicarboxylic acid (Elena Hamciuc *et al.*, 2001).

Synthesis of polymers

The polycondensation reaction with equimolar amounts of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole with diacid chloride was carried out in N-methylpyrrolidinone (NMP) using pyridine as an acid acceptor (Mariana Dana Iosip *et al.*, 2003). The reaction sequence is shown in scheme 1.

Evaluation of Inhibition Efficiency of the polyamides

Non-Electrochemical Techniques

Weight loss method

The initial weight of the polished mild steel plates were taken. 1M H₂SO₄ was taken in an 100ml beaker and the specimens were suspended in triplicates into the solution using glass hooks. Care was taken to ensure the complete immersion of the plates. After a period of 3 hours the plates were removed, washed with distilled water, dried and weighed. From the initial and final masses of the plates (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 H₂SO₄. The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using the formulas,

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

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

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

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 1000ppm. Activation energy (E_a), Free energy of adsorption (ΔG⁰), Enthalpy and Entropy (ΔH⁰ & ΔS⁰) were calculated using the formula,

$$(i) \quad E_a = -2.303 \times 8.314 \times \text{slope (KJ)}$$

$$(ii) \quad K = \frac{1}{55.5} \exp \left[-\frac{\Delta G^{\text{ads}}}{RT} \right]$$

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

θ - Surface coverage of the inhibitor, C- concentration of inhibitor in ppm.

$$(iii) \quad CR = \left[\frac{RT}{Nh} \right] \exp \left[\frac{\Delta S^{\text{ads}}}{R} \right] \exp \left[\frac{\Delta H^{\text{ads}}}{RT} \right]$$

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

Gasometry

Mild steel plates of size 1cm x 3cm x 0.1cm were given fine mechanical polishing and degreased with trichloroethylene. The plates were stored in a desiccator. The plate was suspended from a hook on a glass stopper and introduced into the gasometric cell containing 100ml of 1M H₂SO₄. The temperature was maintained constant throughout the experiments at 303±1K 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 concentrations 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

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

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 polyamides in 1M H₂SO₄ after exposing the mild steel specimen for 3hours. From the amount of dissolved iron, the inhibitor efficiency was calculated.

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

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

Electro chemical Techniques

The electrochemical measurements were performed in a classical three-electrode cell assembly with mild steel rod (exposed area 0.785cm²) as working electrode, a platinum electrode and saturated calomel electrode as counter and reference electrodes. The measurements were carried out with IVIUM Compactstat Potentiostat/ Galvanostat. EIS measurements were carried out at a frequency range of 10 KHz to 0.01Hz with a superimposed sine wave of amplitude 10mV. From the plot of Z¹Vs Z¹¹ the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated.

$$I.E (\%) = \frac{R_t^* - R_t}{R_t^*} \times 100$$

Where, R_t and R_t^{*} 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 1mV/s. The data were collected and analyzed by IVIUM Soft software.

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

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 1ppm KCl/KBr/KI to the mild steel specimen immersed in 1M H₂SO₄ containing various concentrations of the inhibitors for a 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 H₂SO₄ in the presence and absence of the inhibitors using Medzer biomedical research microscope (Mumbai, India).

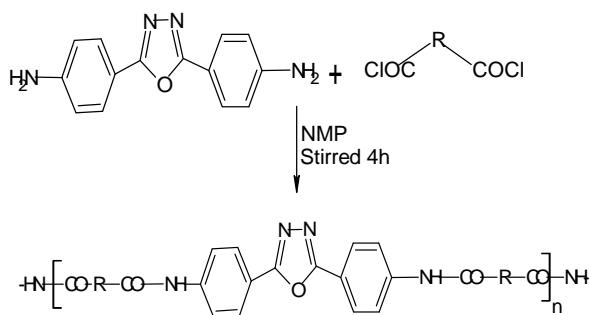
RESULTS AND DISCUSSION

Weight loss measurements

Table 2 gives the values of inhibition efficiency (%IE) for different concentrations of the polyamides in 1M H₂SO₄. The above results are plotted in (Fig 2). It can be seen from this

table that the polyamides efficiently inhibits the corrosion of mild steel in 1M H₂SO₄. The corrosion rate decreased considerably with an increase in concentration of the inhibitor. This is due to the presence of heteroatoms like nitrogen, oxygen and aromatic rings. The extent of inhibition depends upon the nature and mode of adsorption of inhibitor on the metal surface. The adsorption is assumed to be quasi substitution process between the water molecules on the surface and the organic molecules. The polyamides may get adsorbed on the mild steel surface by flat orientation with -NH-CO- and aromatic rings as anchoring groups.

Scheme 1



[1-7]

Compound	NAME	R
1.	ATP1	(C ₆ H ₄)
2.	ASC2	(CH ₂) ₂
3.	AML3	(CH ₂) ₃
4.	AAP4	(CH ₂) ₄
5.	APM5	(CH ₂) ₅
6.	ASB6	(CH ₂) ₆
7.	AAZ7	(CH ₂) ₇

The structures of the synthesized polymers are given in (Table1) and they were confirmed by IR spectra (Fig 1)

The inhibitor ATP1 exhibited maximum inhibition efficiency of 94% at a concentration of 1000ppm. This is higher than the other inhibitors, which may be attributed to the presence of additional phenyl groups as anchoring sites in their structure. The order of inhibition efficiency for the other polyamides is AAZ7>ASB6>APM5>AAP4>AML3>ASC2. The length of alkyl chain increases in the reverse order. As the length of the alkyl chain increases -(CH₂)₂, (CH₃)₃, (CH₄)₄, (CH₅)₅, (CH₆)₆ and (CH₇)₇ the electron density on the nitrogen and oxygen atoms and aromatic rings increases due to the +I effect, which facilitates stronger adsorption of AAZ7 on the mild steel surface. This leads to higher inhibition efficiency of AAZ7 in comparison with other polyamides. The better coverage of the higher alkyl group also plays a major role for better adsorption on the mild steel surface than the lower chain alkyl groups (Sadaf Khan *et al.*, 2010).

Effect of Temperature

The effect of temperature on the inhibited acid-metal reaction is highly complex because many changes occur on the metal surface such as rapid etchings, desorption of the inhibitor and decomposition or rearrangement of inhibitor. To evaluate the effect of temperature on the adsorption behaviour and to determine the thermodynamic parameters, weight loss measurements were carried out in the temperature range 303-313K and the results are presented in (Table 3).

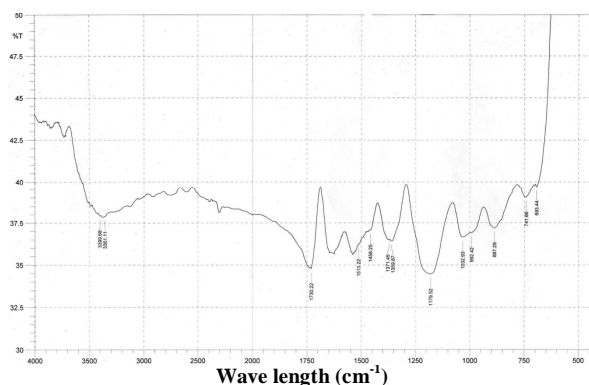


Fig 1 IR Spectrum of ATP1

The data reveal that as the temperature is increased the corrosion rate increased and inhibition efficiency decreased. The decrease in the inhibition efficiency with increase in temperature may be attributed to the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction (E.E.Ebenso *et al.*, 2008; S.Chitra *et al.*, 2011). The corrosion rate (CR) of the mild steel in acidic media is related to temperature by the Arrhenius equation.

$$\log CR = \log A - E_a / 2.303RT \text{----- (1)}$$

where E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The plot of log CR Vs 1/T is depicted in (Fig 3). Values of E_a ranged from 53.70 to 84.80J/mole (Table 4).

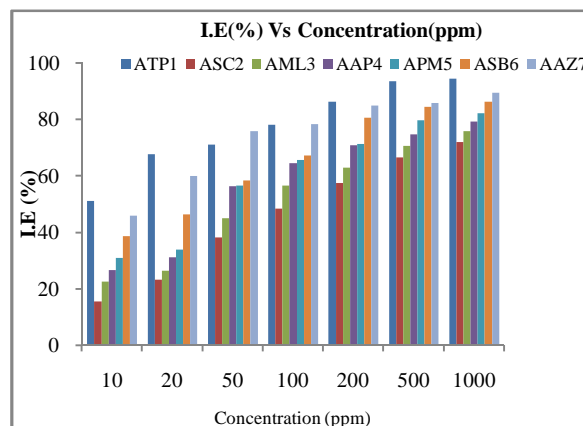


Fig 2 Plot of inhibition efficiency (%) Vs concentration (ppm) for the inhibition of corrosion of mild steel in 1M H₂SO₄

These values are higher than the value of 37.36J/mole obtained for blank indicating that the corrosion reaction of mild steel is retarded by the polyamides (E.E.Ebenso, 2003). It also supports the phenomenon of physical adsorption. The free energy of adsorption (ΔG⁰_{ads}) was calculated from the equilibrium constant of adsorption at different temperatures using the following equation:

$$\Delta G^0_{ads} = -RT \ln (55.5k) \text{----- (2)}$$

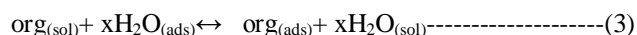
The negative values of ΔG⁰_{ads} (Table 4) are constituent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. Generally values of ΔG⁰_{ads} up to -40 kJ/mole are consistent with electrostatic interaction between charged molecule and a charged metal which indicates physisorption while those more negative than -40 kJ/mole involve charge sharing or transfer

from the inhibitor molecules to the metal surface to form a coordinate type of bond which indicates chemisorption (Quarshi *et al.*, 2002; Libin Tang *et al.*, 2003; Tebbji *et al.*, 2007). The values of ΔG_{ads}^0 in our measurements ranged from -35 to -25 kJ/moles. Thus the adsorption of the polyamides on steel in 1M H₂SO₄ is neither physisorption nor chemisorption but a combination of both in which physisorption predominates. The negative values of ΔH^0 (Table 4) also show that the adsorption of the inhibitor is an exothermic process (Gomma *et al.*, 1995) 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 (Durnie *et al.*, 1999). In an exothermic process, physisorption is distinguished from chemisorption from ΔH^0 value which would be lower than 40 kJ/mole while ΔH^0 value for a chemisorption process approaches 100kJ/moles (Martinez *et al.*, 2002). In the present case ΔH^0 values range from -117.46 to -213.47 kJ/mole proving that a comprehensive adsorption (physical and chemical adsorption) might occur.

adsorbed onto the steel surface, as a result a decrease in entropy results (Tebbj *et al.*, 2011).

Adsorption isotherm

The interaction between the inhibitors and the steel surface can be described by the adsorption isotherm. During corrosion inhibition of metals the nature of the inhibitor on the corroding surface has been deduced in terms of adsorption characteristics of the inhibitor. Furthermore, the solvent (H₂O) molecules could also be adsorbed at metal/solution interface. So the adsorption of the organic inhibitor molecules from aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [org_(sol)] and water molecules at the electrode surface [H₂O_(ads)] (Sahin *et al.*, 2002).



where 'x' is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. The polyamides contain repeated oxadiazole moiety, benzene rings and -CO-NH- linkages.

Table 1 Structure of the polyamides

S.NO	Structure of the polymers	Yield (%)
1.	<p style="text-align: center;">ATPI</p>	88
2.	<p style="text-align: center;">ASC2</p>	65
3.	<p style="text-align: center;">AML3</p>	68
4.	<p style="text-align: center;">AAP4</p>	80
5.	<p style="text-align: center;">APM5</p>	85
6.	<p style="text-align: center;">ASB6</p>	82
7.	<p style="text-align: center;">AAZ7</p>	85

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

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between the degree of surface coverage (θ) and inhibitor concentration (C) must be found.

Table 2 Inhibition efficiencies of various concentrations of the inhibitors for corrosion of mild steel in 1M H₂SO₄ obtained by weight loss measurement at 30±1°C

Name of the inhibitors	Concentration (ppm)	Weight loss (g)	Inhibition Efficiency (%)	Degree of surface coverage(θ)	Corrosion rate (mpy)	
Blank	-	0.2209	-	-	92655.25	
	ATP1	10	0.1084	50.93	0.5093	45467.76
		20	0.0714	67.68	0.6767	29948.32
		50	0.0639	71.07	0.7107	26802.49
		100	0.0486	77.99	0.7799	20384.99
		200	0.0306	86.15	0.8615	12835.00
		500	0.0145	93.44	0.9344	6081.94
		1000	0.0126	94.30	0.9430	5284.99
ASC2	10	0.1869	15.39	0.1539	78394.14	
	20	0.1697	23.18	0.2318	71179.70	
	50	0.1369	38.03	0.3803	57421.93	
	100	0.1144	48.21	0.4821	47984.43	
	200	0.0944	57.27	0.5727	39595.54	
	500	0.0742	66.41	0.6641	31122.77	
	1000	0.0623	71.80	0.7180	26131.38	
AML3	10	0.1712	22.50	0.2250	71808.87	
	20	0.1628	26.30	0.2630	68285.53	
	50	0.1219	44.82	0.4482	51130.26	
	100	0.0962	56.45	0.5645	40350.54	
	200	0.0820	62.88	0.6288	34394.43	
	500	0.0652	70.48	0.7048	27347.77	
	1000	0.0536	75.74	0.7574	22482.21	
AAP4	10	0.1623	26.53	0.2653	68075.81	
	20	0.1522	31.10	0.3110	63839.42	
	50	0.0968	56.18	0.5618	40602.21	
	100	0.0786	64.42	0.6442	32968.32	
	200	0.0648	70.67	0.7067	27179.99	
	500	0.0564	74.47	0.7447	23656.66	
	1000	0.0459	79.22	0.7922	19252.49	
APM5	10	0.1531	30.74	0.3074	64174.98	
	20	0.1462	33.82	0.3382	61322.76	
	50	0.0964	56.36	0.5636	40434.43	
	100	0.0759	65.64	0.6564	31835.82	
	200	0.0634	71.30	0.7130	26592.77	
	500	0.0452	79.54	0.7954	18958.88	
	1000	0.0393	82.21	0.8221	16484.16	
ASB6	10	0.1357	38.57	0.3857	56918.59	
	20	0.1186	46.31	0.4631	49746.09	
	50	0.0922	58.26	0.5826	38672.77	
	100	0.0726	67.13	0.6713	30451.66	
	200	0.0433	80.40	0.8040	18161.94	
	500	0.0346	84.34	0.8433	14512.77	
	1000	0.0304	86.24	0.8624	12751.11	
AAZ7	10	0.1196	45.86	0.4586	50165.54	
	20	0.0888	59.80	0.5980	37246.65	
	50	0.0538	75.65	0.7564	22566.10	
	100	0.0483	78.13	0.7813	20259.16	
	200	0.0337	84.74	0.8474	14135.27	
	500	0.0316	85.69	0.8569	13254.44	
	1000	0.0233	89.45	0.8945	9773.05	

Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm. The Langmuir isotherm is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites whether occupied or not (Avci, 2008). According to this isotherm, θ is related to C by

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (4)$$

where K_{ads} is the equilibrium constant of the adsorption process. Fig 4 shows the plots of C/θ against C at 303K. A straight line was obtained suggesting that the adsorbed inhibitor molecules form monolayer on the mild steel surface and there is no interaction among the adsorbed inhibitor molecules (Ebenso *et al.*, 2010).

Electrochemical Measurements

Polarization studies

Polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. Polarization curves of mild steel in 1M H₂SO₄ solutions without and with different concentrations of AAP4 are shown in (Fig 5). The anodic and cathodic current potential curves are extrapolated up to their intersection at a point where corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are obtained (Abd *et al.*, 1999). Table 5 shows the electrochemical parameters I_{corr}, E_{corr}, b_a and b_c obtained from Tafel plots. From Table 5 it is evident that increasing the concentration of the polyamides reduces both the cathodic and anodic currents and there is no definite trend in the shift of E_{corr} values.

Table 3 Inhibition efficiencies of 1000 ppm concentrations of the inhibitors for corrosion of mild steel in 1M H₂SO₄ obtained by weight loss measurement at higher temperature

Name of the inhibitor	Temperature (K)	Weight loss(g)	Inhibition efficiency (%)	Corrosion rate(mpy)
Blank	303	0.0736	-	92606.3
	313	0.1350	-	169862.1
	323	0.1979	-	249005.3
	333	0.2846	-	358094.5
ATP1	303	0.0041	94.4	5158.8
	313	0.0128	90.5	16105.5
	323	0.0312	84.2	39257.0
	333	0.0885	68.9	111354.1
ASC2	303	0.0359	51.2	45170.8
	313	0.0924	31.6	116261.2
	323	0.1632	17.5	205344.4
	333	0.2484	12.7	312546.3
AML3	303	0.0278	62.2	34979.0
	313	0.0638	52.7	80275.6
	323	0.1425	28.0	179298.9
	333	0.2316	18.6	291407.9
AAP4	303	0.0178	75.8	22396.6
	313	0.0502	62.8	63163.6
	323	0.1187	40.0	149352.9
	333	0.1993	30.0	250766.8
APM5	303	0.0121	83.6	15224.7
	313	0.0365	73.0	45925.7
	323	0.0908	54.1	114248.0
	333	0.1898	33.3	238813.6
ASB6	303	0.0101	86.2	12708.2
	313	0.0289	78.6	36363.1
	323	0.0614	69.1	77255.2
	333	0.1727	39.3	217297.7
AAZ7	303	0.0077	89.6	9688.4
	313	0.0223	83.5	28058.7
	323	0.0502	74.6	63163.6
	333	0.1222	57.1	153756.7

Table 4 Kinetics/Thermodynamic Parameters of mild steel corrosion in 1M H₂SO₄

Name of the inhibitor	E _a (J)	-ΔG ⁰ _{ads} (kJ)				-ΔH ⁰ kJ/mole	-ΔS ⁰ kJ/mole
		303 K	313 K	323K	333 K		
Blank	37.36	-	-	-	-	-	-
ATP1	84.80	34.66	34.31	33.84	32.45	135.83	0.8532
ASC2	53.70	27.65	26.42	25.18	24.92	183.24	1.1513
AML3	60.25	28.78	28.72	26.80	26.17	187.52	1.1346
AAP4	68.26	30.40	29.80	28.25	27.90	175.01	1.0671
APM5	77.09	31.62	31.02	29.78	28.33	213.47	1.1671
ASB6	77.67	32.15	31.82	31.49	29.05	183.39	1.0544
AAZ7	83.27	32.95	32.65	32.24	31.04	117.46	0.8259

Table 5 Corrosion parameters for corrosion of mild steel with selected concentrations of the inhibitors in 1M H₂SO₄ by potentiodynamic polarization method

Name of the inhibitor	Concentration (ppm)	Tafel slopes(mV/dec)		E _{corr} (mV)	I _{corr} (μAmp/cm ²)	Inhibition efficiency (%)
		b _a	b _c			
Blank	-	52	112	-467.4	1569	-
	10	50	122	-488.2	1053	32.9
ATP1	100	34	177	-451.3	990	36.9
	1000	43	169	-450.3	268.3	82.9
ASC2	10	53	119	-485.2	1029	34.4
	100	39	111	-469.9	738.3	52.9
AML3	1000	39	163	-442.6	666.9	57.5
	10	56	123	-490.1	1225	21.9
AAP4	100	48	131	-484.1	1145	27.0
	1000	37	151	-463.3	536.3	65.8
APM5	10	66	103	-514.3	1275	18.7
	100	52	152	-483.3	834.5	46.8
ASB6	1000	37	115	-469.9	343.6	78.1
	10	79	121	-501.8	1009	35.7
AAZ7	100	47	110	-497	865.3	44.9
	1000	61	122	-485.9	336.4	78.6
ASB6	10	42	137	-480.3	1315	16.2
	100	44	122	-472.9	1059	32.5
AAZ7	1000	32	147	-455.1	300.2	80.9
	10	67	99	-518.9	1396	11.0
AAZ7	100	50	107	-504	1040	33.7
	1000	32	148	-468.2	287.6	81.7

Table 6 AC-impedance parameters for corrosion of mild steel for selected concentrations of the inhibitors in 1M H₂SO₄

Name of the inhibitor	Concentration (ppm)	R _i (ohm cm ²)	C _{dl} (μF/cm ²)	Inhibition efficiency (%)
Blank	-	11.06	27.8	-
ATP1	10	33.77	22.9	67.25
	100	53.47	19.5	79.32
	1000	73.22	21.5	85.0
ASC2	10	11.56	19.9	4.33
	100	18.56	12.5	40.41
	1000	25.53	28.4	56.68
AML3	10	13.62	21.5	18.80
	100	29.43	15.1	62.42
	1000	32.45	12.2	65.92
AAP4	10	20.8	25.2	46.83
	100	31.22	23.2	64.57
	1000	50.32	21.2	78.02
APM5	10	23.41	17.4	52.76
	100	25.68	16.3	56.93
	1000	51.36	18.8	78.47
ASB6	10	30.49	23.4	63.73
	100	39.16	15.3	71.76
	1000	60.97	14.0	81.86
AAZ7	10	36.52	24.3	69.72
	100	53.87	21.3	79.47
	1000	69.29	23.0	84.04

Table 7 Synergistic effect of 1ppm KCl / KBr / KI on the inhibition efficiency of inhibitors by weight loss method at 30±1°C

Name of the inhibitor	Concentration (ppm)	Inhibition efficiency (%)			
		Without KCl, KBr and KI	With 1ppmKCl	With 1ppmKBr	With 1ppm KI
ATP1	1	25.3	28.6	30.4	38.6
	10	29.4	31.2	34.1	46.7
	30	36.5	37.5	38.9	55.4
	50	55.8	56.8	59.4	66.7
	100	75.2	78.4	82.6	88.7
ASC2	1	15.3	24.7	28.3	36.7
	10	22.7	26.4	33.5	39.5
	30	27.6	36.5	39.2	45.2
	50	32.4	42.8	46.5	58.6
	100	47.1	52.0	64.3	72.5
AML3	1	12.3	27.6	34.5	46.5
	10	19.2	33.4	42.8	49.8
	30	27.6	38.6	49.6	59.7
	50	34.8	42.9	57.4	68.2
	100	52.6	66.8	70.6	79.6
AAP4	1	22.8	36.5	41.9	45.3
	10	24.9	42.6	51.8	56.1
	30	40.2	48.7	58.7	63.8
	50	55.4	58.6	66.3	76.4
	100	62.9	70.2	76.4	88.7
APM5	1	25.8	33.6	37.4	45.8
	10	29.6	38.4	43.9	53.6
	30	34.2	43.5	52.8	69.8
	50	41.4	51.6	67.2	72.8
	100	62.3	66.7	78.3	87.2
ASB6	1	21.5	30.2	42.8	55.6
	10	28.6	38.6	51.1	68.4
	30	34.9	49.1	62.3	71.8
	50	54.8	58.3	70.5	78.9
	100	68.9	75.8	78.6	88.9
AAZ7	1	22.6	29.3	38.5	45.2
	10	29.4	38.9	47.6	56.3
	30	46.4	48.6	62.1	73.6
	50	62.9	67.9	76.4	82.6
	100	74.8	79.2	84.6	90.2

Table 8 Amount of dissolved iron present in the corrosive solution with and without inhibitors in 1M H₂SO₄ measured using atomic absorption spectrophotometer

Name of the inhibitor	Concentration (ppm)	Amount of iron content (mg/l)	Inhibition efficiency (%)
	Blank	1304.96	-
ATP1	10	649.42	50.23
	1000	66.98	94.89
AAZ7	10	712.82	45.38
	1000	194.63	85.09

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 i.e., they reduce anodic dissolution and also retard cathodic hydrogen evolution reaction.

Electrochemical impedance spectroscopy

Mechanism of inhibition

The polyamides exhibit good inhibition efficiency which may be attributed to the flat orientation of the polyamides on the mild steel surface. From ΔG°_{ads} values it has been confirmed that adsorption of the polyamides on the mild steel surface is a combination of physisorption and chemisorption. The corrosion inhibition of mild steel by polyamides is due to the adsorption at the electrode/solution interface. The polyamides contain repeated oxadiazole moiety, benzene rings and -CO-NH- linkages.

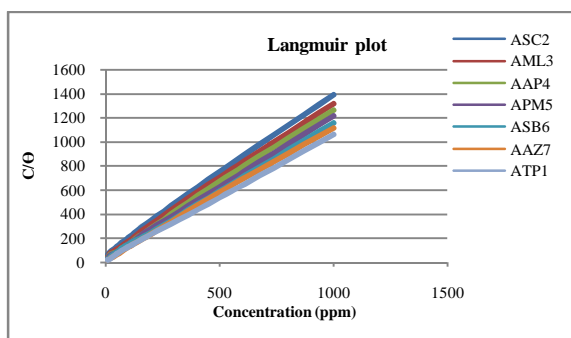


Fig 4 Langmuir plot of inhibitors in 1M H₂SO₄

The presence of hetero oxygen, nitrogen atoms in the structure makes possible its adsorption by i) electrostatic interaction between the positively charged Nitrogen atom of the oxadiazole ring and negatively charged metal surface ii) interaction of π -electrons of the aromatic rings with metal surface iii) co-ordinate type linkage through the transfer of lone pairs of electrons of oxygen and nitrogen atoms of the amide -CO-NH- linkage to the steel surface, giving a stable chelate with ferrous ions.

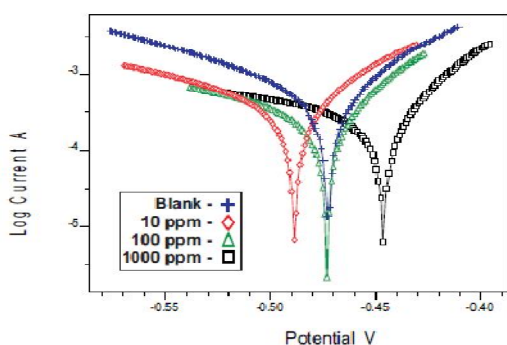


Fig 5 Polarization curves for mild steel recorded in 1M H₂SO₄ of selected concentrations of the inhibitor (AAP4)

The simultaneous adsorption of the oxygen and nitrogen atoms of the -CO-NH- group forces the polyamide molecule to be horizontally oriented at the metal surface, which lead to an increase in the surface coverage and consequently protection efficiency (Abdallah, 2004). The corrosion behavior of mild steel in acidic solution in the presence of polyamides was investigated by EIS at $30 \pm 1^{\circ}\text{C}$. Nyquist plots of mild steel in uninhibited and inhibited acidic solutions containing various concentrations of AAP4 displayed one capacitive arc (Fig 6).

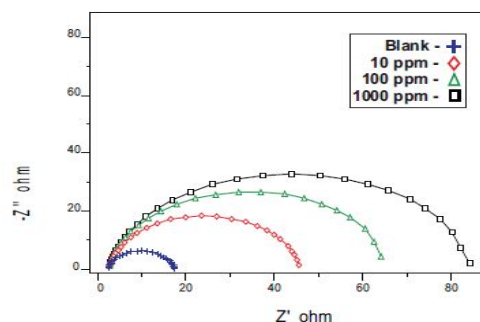
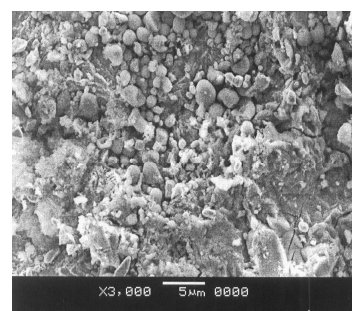


Fig 6 Nyquist diagram for mild steel in 1M H₂SO₄ for selected concentrations of inhibitor (AAP4)

The impedance parameters derived from the Nyquist plots are given in the Table 6. From Table 6, it is clear that as concentration of the inhibitor increases charge transfer resistance R_{ct} increases and double layer capacitance C_{dl} decreases. Decrease in C_{dl} is due to an increase in the thickness of the electrical double layer. This suggests that the inhibitor molecules function by adsorption at the metal solution interface.

Synergism

The synergistic effect provided by the addition of halide ions I^- , Br^- and Cl^- to the solutions containing 1M H₂SO₄ and the polyamides 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 $\text{I}^- > \text{Br}^- > \text{Cl}^-$. The highest synergistic influence exhibited by iodide ion may be explained as follows. The steel surface is originally positively charged in 1M H₂SO₄.

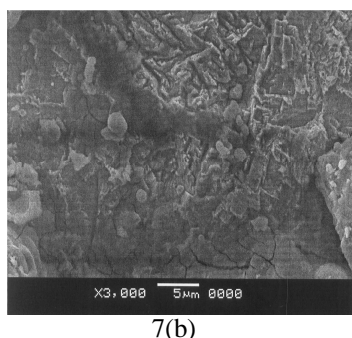


7(a)

When I^- is added to the inhibiting solution they are strongly chemisorbed by forming chemical bonds even leading to the formation of iron halide (Saratha *et al.*, 2002). This strong chemisorption of I^- ions shift Φ_n of the metal to more positive potential than Cl^- and Br^- and renders the surface more 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 $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

Atomic Absorption Spectrophotometric Studies (AAS)

The inhibitor efficiency (%) of the polyamides ATP1 and AAZ7 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.



7(b)

Fig 7(a&b) Scanning electron microscopy photographs in the absence (a) and presence of inhibitor (b)

Surface Morphology

The mild steel specimens immersed in the blank acid (1M H₂SO₄) and inhibited acid (1M H₂SO₄ + 1000ppm of AAZ7) were observed under a scanning electron microscope and the photographs are shown in Figs 7(a&b) respectively. The photographs show that the mild steel was heavily corroded in 1M H₂SO₄ (Fig 7a) where as in the presence of inhibitor the surface condition was comparatively better (Fig7b). This suggests the presence of protective adsorbed layer of inhibitor molecules on the mild steel surface which reduces the corrosion rate of the metal appreciably.

CONCLUSIONS

The conclusions arrived based on the investigations are

- The order of inhibition efficiency of the synthesized compounds is ATP1>AAZ7>ASB6>APM5>AAP4>AML3>ASC2.
- All investigated inhibitors are effective inhibitors for corrosion of mild steel in 1M H₂SO₄.
- 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.
- The less negative values of ΔG^o_{ads} indicate the spontaneous adsorption of the inhibitors on the metal surface.
- 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.

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