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Benzodiazepine derivatives as corrosion inhibitors for mild steel in sulphuric acid medium

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ABSTRACT

4-(2-hydroxy phenyl)-2-phenyl-2,3-dihydro-1H-1,5-benzo diazepine(SATD),4-(2-hydroxy phenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (SAD), 4-methyl-2-phenyl-2,3-dihydro-1H-1,5-benzodiazepine (BAD) were synthesized by the condensation of o-phenylenediamine and chalkones and characterized by FTIR spectra. Corrosion inhibition property on mild steel in sulphuric acid medium of the benzodiazepines was investigated by weight loss and electrochemical method. Scanning electron microscopic studies (SEM) were carried out to study the surface morphology of the inhibited and uninhibited metal samples. The results showed that inhibition efficiency of the inhibitors depended on concentration of inhibitor and temperature. The thermodynamic parameters such as E_a, ΔG^0, ΔH^0, ΔS^0 *have been evaluated. The inhibition efficiency has been synergistically enhanced by the addition of halide ions.*

Keywords: mild steel, benzodiazepine, corrosion inhibitors.

INTRODUCTION

Corrosion is the destruction of metals by reaction with environment. Mild steel is used in many industries due to its good structural properties, mechanical workability and low cost [1]. Use of acids is also common in industries for pickling and descaling of metallic components. Due to the corrosive nature of acids, mild steel undergoes corrosion and leads to great economic loss. In such situation inhibitors are used to mitigate corrosion. Organic compounds containing heteroatom (N, O, S and P) and aromatic rings are used for this purpose [2]. These compounds get adsorbed on the metal surface to form a protective layer which prevents the metal from acid attack.

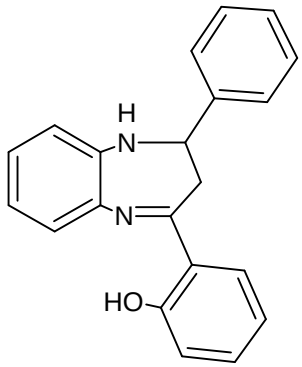
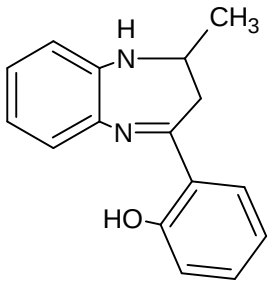
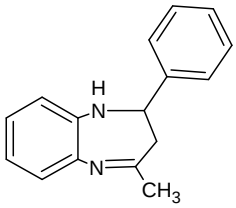
Compounds with benzodiazepine scaffolds have recently received considerable attention for their pharmacological properties. Many members of benzodiazepine are widely used as anti anxiety, analgesic, sedative and hypnotic agents [3]. Though many reports are available on the synthesis of benzodiazepines as biological agents, limited studies are reported on their use as corrosion inhibitors [4].

The aim of this investigation was to synthesize three benzodiazepine derivatives and to evaluate their inhibition efficiency on the corrosion of mild steel in 1M H_2SO_4 using gravimetric and electrochemical techniques and by quantum chemical calculations.

MATERIALS AND METHODS

2.1. Synthesis of benzodiazepines

The 1, 5-benzodiazepines were synthesized by the condensation of o-phenylenediamine with chalkones under solvent free conditions catalyzed by sulphated zirconia [5].

S. NO.	Structure of the compounds	IUPAC Name
1.		4-(2-hydroxyphenyl)-2-phenyl-2,3-dihydro-1H-1,5-benzodiazepine (SATD)
2.		4-(2-hydroxyphenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (SAD)
3.		4-methyl-2-phenyl-2,3-dihydro-1H-1,5-benzodiazepine (BAD)

The synthesized compounds were characterized by FTIR spectra

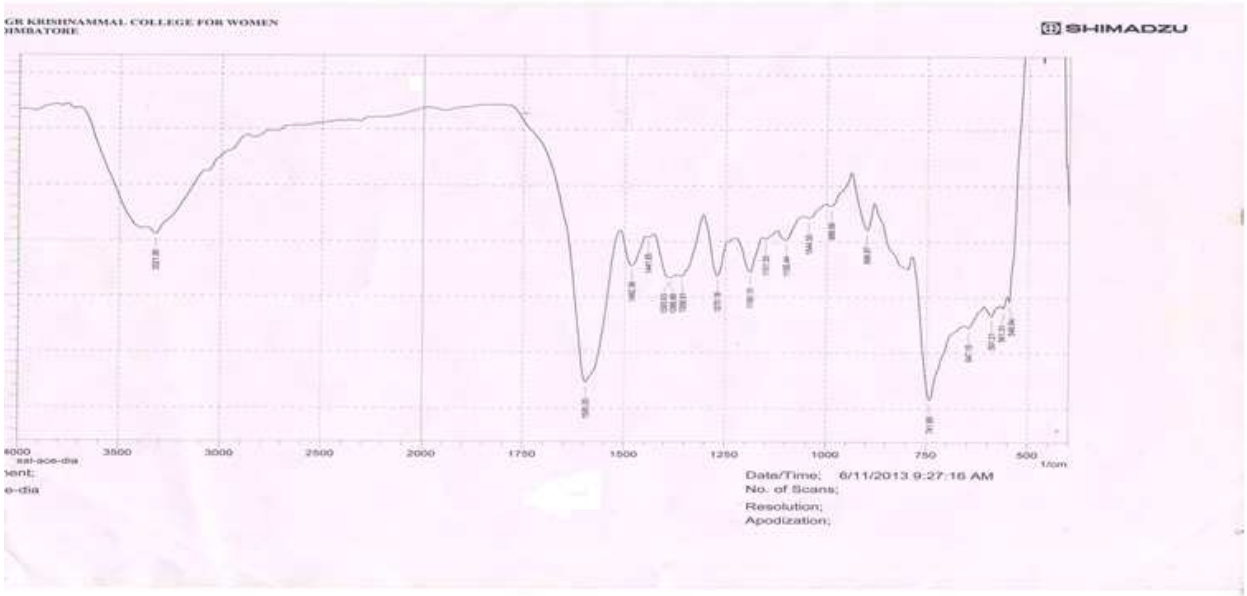


Figure1. FTIR Spectrum of SATD

FTIR spectra: 1624 cm^{-1} (C= N), 3321 cm^{-1} (-N-H), 1396 cm^{-1}(-OH) stretching

2.2. Material preparation

Mild steel specimens of dimensions 1 cm X 3 cm X 0.1 cm having composition 0.084% C, 0.369% Mn, 0.129% Si, 0.025% S, 0.022% Cr, 0.011% Mo, 0.015% Ni and rest iron were used for weight loss measurements. A mild steel

rod of same composition with exposed area 0.785 cm^2 was used for electrochemical measurements. The specimens were polished with 100, 120 and 180 grades emery Sheets, rinsed with double distilled water, degreased with acetone and dried. The plates were then kept in a desiccator to avoid contact with moisture.

2.3. Weight loss Measurements:

The mild steel coupons were weighed and then immersed in triplicate in 1M H_2SO_4 (100 ml) without and with various concentration of the inhibitors. After 3h of immersion the coupons were removed, washed with double distilled water, dried and weighed. From the initial and final weights of the specimen the average weight loss of the triplicate specimens was recorded. The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using the formula,

$$\text{Efficiency of inhibitor} = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

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

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

Where, Θ is the surface coverage. The above procedure was repeated at different temperatures (313-333K).

2.4. Electrochemical Techniques

Electrochemical studies were performed on IVIUM compactstat using conventional three electrode cell with mild steel rod as working electrode. The response of the electrochemical system to AC excitation with a frequency ranging from 10 KHz to 0.01 KHz and peak to peak amplitude of 10 mV was measured. From the plot, 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 polarisation curves were potentiodynamically obtained at open circuit potential (OCP) with a potential range of -200 mV to +200 mV (versus OCP) at a scan rate of 1 mV / s.

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

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

2.5. Surface Morphology:

Surface studies of mild steel specimens were carried out to understand the morphology of mild steel in 1M H_2SO_4 in the presence and absence of the inhibitor using Medzer biomedical research microscope (Mumbai, India).

2.6. Synergism study:

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 inhibitor for a duration of three hours. From the weight loss the inhibition efficiency was calculated.

RESULTS AND DISCUSSION

3.1. Weight loss Measurements:

The data clearly show that the corrosion rate decreased markedly in the presence of inhibitors. This is due to the increase of surface coverage (Θ) by the inhibitor molecules on the metal through adsorption. At 0.5 mM concentration the efficiency reached >95% which shows that the benzodiazepines are excellent inhibitors for mild steel corrosion in H_2SO_4.

Table1. Inhibition efficiencies of various concentrations of the inhibitor for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurement at 30±1^{0}C

Inhibitor	Concentration (mM)	Weight loss (g)	Inhibition Efficiency (%)	Degree of surface coverage(Θ)	Corrosion rate (mpy)
BLANK		0.2656	-	-	17466.71
SATD	0.1	0.0898	66.18	0.6618	5905.53
	0.2	0.056	78.91	0.7891	3682.74
	0.3	0.0142	94.65	0.9465	933.83
	0.4	0.0085	96.79	0.9677	558.98
	0.5	0.0030	98.87	0.9887	197.28
SAD	0.1	0.1295	51.24	0.5124	8516.33
	0.2	0.1122	57.75	0.5775	7378.63
	0.5	0.0450	83.05	0.8305	2959.34
BAD	0.1	0.1462	44.95	0.4495	9614.58
	0.2	0.1372	48.34	0.4834	9022.71
	0.3	0.1232	53.61	0.5361	8102.02
	0.4	0.0812	69.42	0.6942	5339.97
	0.5	0.0600	77.40	0.7740	3945.76

3.1.1. Adsorption isotherm

The mechanism of adsorption and the surface behavior of organic molecules can be studied using adsorption isotherms. The surface coverage (Θ) values were tested by fitting in to Langmuir isotherm and is expressed as

$C/\Theta = 1/K_{ads} + C$

Where C is the concentration of the inhibitor and K_{ads} is the adsorption equilibrium. Figure 2 represents the Langmuir isotherm for SATD. K_{ads} is related to standard free energy of adsorption as,

$\Delta G^{\circ}_{ads} = -RT \ln (55.5\ K_{ads})$

Where, 55.5 is the molar concentration of water. The value of ΔG°_{ads} is negative and less than - 40 KJ/mole (Table3) suggesting that the adsorption of the studied benzodiazepines are spontaneous and involves electrostatic interaction with the mild steel surface [6].

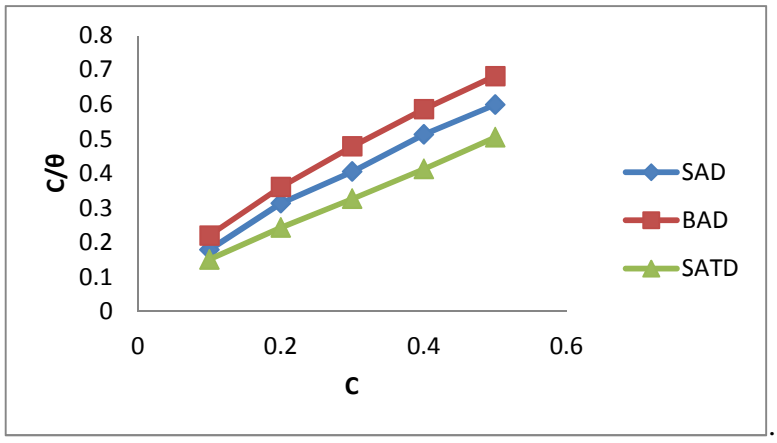


Figure 2. Langmuir adsorption isotherm plots of benzodiazepine

3.1.2. Effect of Temperature:

The effect of temperature on corrosion and inhibition was evaluated using weight loss measurements in the temperature range 30- 60° C and the data are given in Table2.

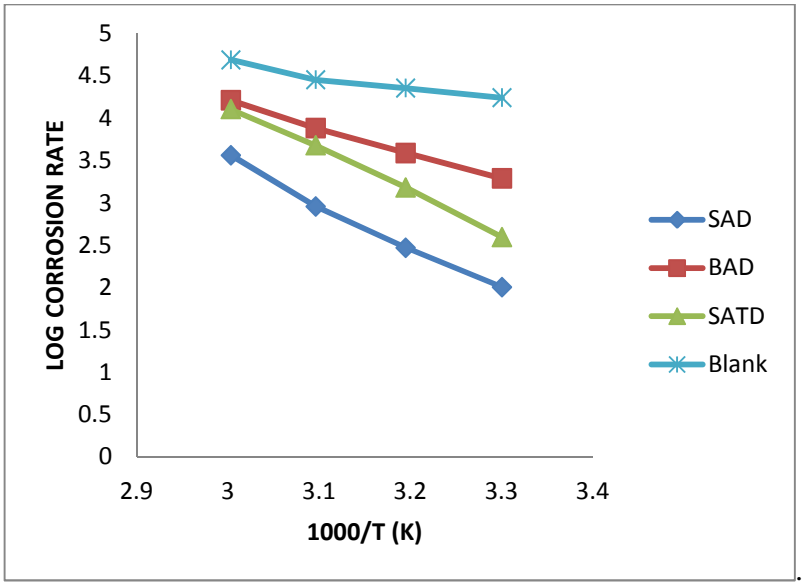


Figure3. Arrhenius plot of corrosion of mild steel in 1M H_2SO_4 solution in the absence and presence of inhibitors

Table2. Inhibition efficiency of the inhibitors for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurement at higher temperatures

Inhibitor concentration: 0.5mM

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mpy)
BLANK	303	0.0609	-	76627.43
	313	0.1152	-	144950
	323	0.1443	-	181565.5
	333	0.2486	-	312801
SATD	303	0.001	98.87	197.28
	313	0.0015	98.30	295.93
	323	0.0046	94.80	907.52
	333	0.0186	78.98	3669.56
SAD	303	0.015	83.05	2959.32
	313	0.02	77.40	3945.76
	323	0.0291	67.11	5741.08
	333	0.0304	65.64	5997.56
BAD	303	0.02	77.40	3945.76
	313	0.035	60.45	6905.08
	323	0.0358	59.54	7062.91
	333	0.0387	56.27	7635.05

The inhibition efficiency decreases with increase in temperature. This behavior is attributed to physical adsorption which is weakened at higher temperature leading to desorption of the adsorbed inhibitor molecules. Hence more surfaces are exposed to acid attack.

Table: 3 Kinetics/Thermodynamic Parameters of mild steel corrosion in1M H_2SO_4

Name of the inhibitor	E_a (J)	ΔG^0_{ads}				ΔH^0 KJ/mole	ΔS^0 KJ/mole
		303K	313K	323K	333K		
BLANK	27.72	-	-	-	-	-12.18	-0.64
SATD	96.33	-23.13	-22.06	-20.44	-9.57	-79.70	-1.81
SAD	71.74	-15.87	-15.46	-13.78	-6.84	-56.6	-1.36
BAD	47.26	-14.96	-14.11	-13.32	-5.73	-14.4	-1.00

The activation energy for corrosion could be calculated from the slopes of plot (log corrosion rate Vs 1/T, Fig 3). E_a values recorded in Table3 for the inhibited solution are found to be higher than that for the blank acid solution. The same phenomenon was observed by several authors and they explained this on the basis of physisorption of the inhibitor [7].

The values of enthalpy and entropy of activation were calculated from the slopes and intercepts of the transition state plot (log corrosion rate/T against 1/T). The slope of straight line is equal to ΔH_{ads} /2.303R and intercept is equal to logR/Nh + ΔS_{ads}/2.303R. The values are recorded in Table3.

The negative ΔH values show that the adsorption of the benzodiazepines on mild steel is an exothermic process. In an exothermic process, physisorption and chemisorption are distinguished from ΔH^0 value. If the value of ΔH^0 is lower than 40 KJ/mole physisorption occurs and for chemisorption process the ΔH^0value approaches 100KJ/mole [8]**.** In the present case ΔH^0 values range from -12.18 to -79.70 KJ/mole suggesting that a comprehensive adsorption (physical and chemical adsorption) might occur. The calculated negative value of ΔS^0 value indicates that the molecules are arranged in an order due to adsorption on to the steel surface.

3.2. Electrochemical Techniques:

3.2.1. Electrochemical impedance Spectroscopy:

Electrochemical impedance spectra for mild steel in 1M H_2SO_4 with and without various concentration of SATD at 30°C are presented as Nyquist plot in Figure4. It is clear that increase in the concentration of the inhibitor results in an increase in impedance of the interface as shown by the increased diameter of the semicircles. The C_{dl} value decreases with increase in inhibitor concentration. The decrease is attributed to the adsorption of organic molecules thereby gradually replacing the water molecules at the surface of the metal and confirms the formation of a protective film.

Table4. AC-impedance parameters for corrosion of mild steel for selected concentrations of the inhibitor in 1M H_2SO_4

Name of the inhibitor	Concentration (mM)	R_{ct} (ohm cm^2)	C_{dl} (μF/cm^2)	IE (%)
BLANK	-			
SATD	0.1	41.48	0.262	65.74
	0.3	60.64	0.165	81.76
	0.5	81.08	0.162	87.43
SAD	0.1	32.14	0.170	65.58
	0.3	98.27	0.257	74.02
	0.5	57.50	0.188	80.76
BAD	0.1	28.90	0.222	61.73
	0.3	54.67	0.259	70.90
	0.5	44.20	0.217	74.97

The corrosion kinetic parameters derived from the Nyquist plots are given in Table4. It is apparent that the presence of all the three inhibitors increases the value of charge transfer resistance of the mild steel in the acidic solution and the effect is more pronounced with SATD.The increase in R_{ct} in the presence of inhibiors is attributed to the formation of protective film of the inhibitor on the metal solution interface[9]**.**

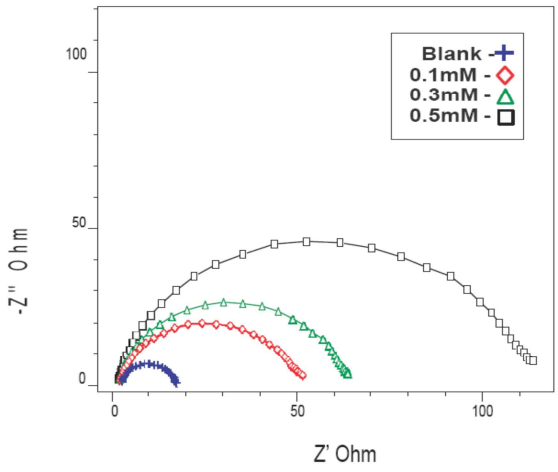


Figure4. Nyquist diagram for mild steel in 1M H_2SO_4 for selected concentrations of inhibitor (SATD)

3.2.2. Polarization Study:

To evaluate the effect of the inhibitors on the electrochemical behavior of mild steel polarization experiments were carried out. The potentiodynamic polarization curves for the corrosion of mild steel in 1M H_2SO_4 in the absence and presence of varying concentrations of the inhibitor are shown in Figure5. The values of electrochemical parameters are given in Table5.

It is observed from the table that E_{corr} values and Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. The inhibitor is said to be cathodic or anodic if the displacement in corrosion potential value of the inhibited solution is greater than 85 mV with respect to uninhibited solution. Considerable shift of E_{corr} value was not observed suggesting that the inhibitors behave as mixed type [10].

Table5. 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	Concentration (mM)	Tafel slopes(mV/dec)		$-E_{corr}$ (mV)	I_{corr} (μAmp/cm^2)	Inhibition efficiency (%)
		b_a	b_c			
BLANK	-	61	137	491.0	414.0	-
SATD	0.1	68	135	495.7	257.0	37.92
	0.3	53	135	477.1	215.3	47.99
	0.5	42	136	461.2	82.3	80.12
SAD	0.1	64	152	491.0	283.5	31.52
	0.3	63	144	484.7	239.0	42.27
	0.5	47	142	468.2	135.6	67.24
BAD	0.1	64	155	491.2	283.5	31.52
	0.3	57	135	483.4	281.8	31.93
	0.5	68	135	495.6	236.0	42.99

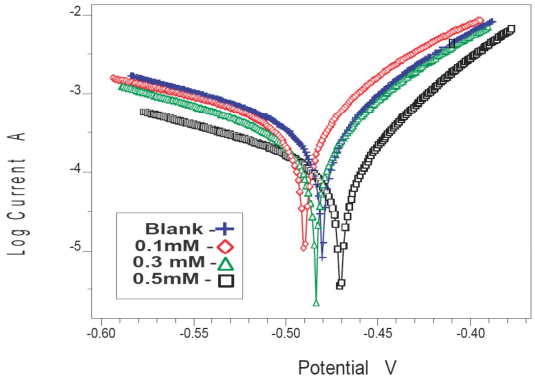


Figure5. Polarization curves for mild steel recorded in 1M H_2SO_4 with selected concentrations of the inhibitor (SATD)

3.3. Surface Morphology

The mild steel specimens immersed in the blank acid (1M H_2SO_4) and inhibited acid (1M H_2SO_4 + 0.5mM of SATD) were observed under a scanning electron microscope and the micro graphs are shown in (Figure 6) and (Figure 7). It is evident that the mild steel was heavily corroded in 1M H_2SO_4 (Figure 6) where as in the presence of inhibitor the surface condition was comparatively better (Figure 7).

Figure 6. SEM image of mild steel in the absence of inhibitor

Figure7. SEM image of mild steel containing 0.5mM of SATD

3.4. Synergism

In order to improve the inhibition performance of an inhibitor and to decrease the amount of inhibitor it is customary to incorporate certain additives such as halides, surfactants etc along with the organic inhibitors. Hence an attempt has been made to study the synergistic effect of addition of halide ions to the solutions containing 1M H_2SO_4 and the benzodiazepines by weight loss method and the data are presented in Table6. Analysis of the data reveals that the addition of halide ions enhanced the inhibition efficiency for all the three inhibitors. It is generally observed that the addition of halide ions increases the adsorption ability of organic cations in acidic solution by forming an interconnecting bridge between the positively charged metal surface and the inhibitor cation I^- shows highest synergistic inhibition. According to Wu *et al*[11], presence of iodide ions causes a more positive shift of potential of zero charge (E_{ocp} - $E_{q=0}$ >0) and makes the overall charge on the metal surface more negative which facilitates the adsorption of positively charged organic species.

Table6. Synergistic effect of 1mM KCl / KBr / KI on the inhibition efficiency of inhibitors by weight loss method at 30±1°C

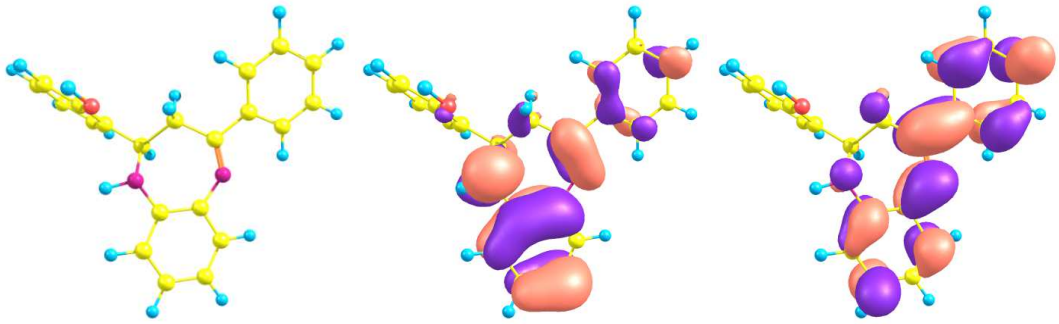
Name of the inhibitor	Concentration (mM)	Inhibition efficiency (%)			
		Without KCl, KBr and KI	With 1mM KCl	With 1mM KBr	With 1mM KI
SATD	0.01	54	52	86	88
	0.03	81	88	94	95
	0.05	89	90	96	96
SAD	0.01	33	47	55	94
	0.03	50	80	89	90
	0.05	57	83	90	91
BAD	0.01	28	33	29	39
	0.03	30	37	35	42
	0.05	35	43	52	49

3.5. Theoretical Calculations

The effect of molecular structure on the inhibition efficiency was studied by Quantum chemical calculations using Gaussian 03 program and all calculations were carried out by complete geometry optimization. The optimized structure E_{HOMO} and E_{LUMO} of SATD were presented in Figure 8. According to Ebenso *et al* [12].,the molecule has a capacity to donate electrons to acceptor molecules if the value of E_{HOMO} is high and the molecule can accept electron easily from the donor molecules if value of E_{LUMO} is low. According to previous quantum chemical studies the increase in inhibition efficiency was facilitated with higher value of dipole moment (μ) and smaller value of ΔE [13].

Table 7. Quantum Chemical parameters for the inhibitors

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	ϰ	μ (D)	η (eV)	σ (eV)
SATD	-5.0619	-1.1676	3.8942	3.1147	4.6546	1.9471	0.5135
SAD	-5.2885	-0.5869	4.7016	2.9377	3.0493	2.3508	0.4253
BAD	-5.3149	-0.6291	4.6858	2.9720	2.7406	2.3429	0.4268



(a) **(b)** **(c)**

Figure 8: (a) Optimized geometry of SATD; (b) E_{HOMO} of SATD (c) E_{LUMO} of SATD

From the results shown in Table 7, SATD was found to be the efficient inhibitor as it possess highest value of E_{HOMO} (-5.0619), lowest value of E_{LUMO} (-1.1676) and highest value of σ (0.5235). Generally it is believed that hard

molecules have large energy gap whereas soft molecules have lower energy gap and are found to be more reactive [14]**.** From all the above calculations done, it is predicted that the inhibitor SATD has lowest energy gap (3.8642 eV) and it can absorb on to the surface of the mild steel more efficiently than SAD and BAD.

3.6. Comparison of inhibition efficiency of the benzodiazepine

The inhibition efficiency of the studied benzodiazepines shows the following order

SATD> SAD> BAD

The trend in inhibition efficiency can be explained by considering the geometry of the compounds. Through single crystal XRD studies Escobar *et al* [15], have reported that the 1, 5-benzodiazepine ring system exhibits a puckered boat like conformation. An intra molecular hydrogen bond between the –OH group and benzodiazepine nitrogen is present as shown,

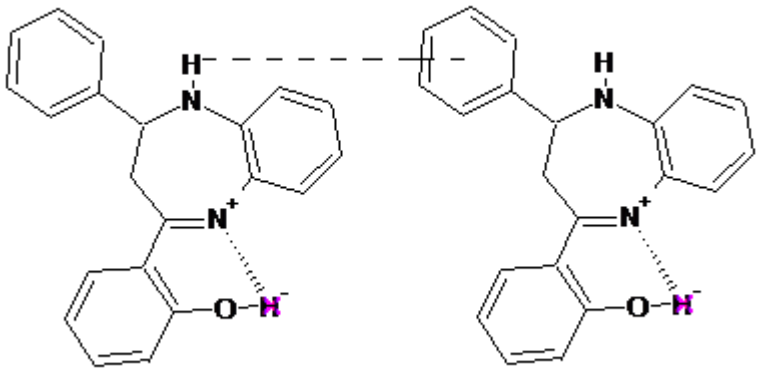


Figure: 9 Intermolecular Hydrogen Bonding

According to Escobar *et al* [15], the intramolecular hydrogen bonding is insensitive to the remainder of the molecule and on the packing mode of the molecule. It is also shown that six membered ring due to the intramolecular hydrogen bonding is planar. An N-H- - π (arene), interaction gives an intermolecular packing which leads to supramolecular chain. The molecular geometry reported by Carlos et al for their studied benzodiazepines can be applied for the present set of benzodiazepines. SATD has a O-H group and forms intramolecular hydrogen bonding to give a planar six membered ring at C2 of the benzodiazepine ring and an intermolecular N-H- - -π (Phenyl) which gives a supramolecular chain. Due to this SATD forms a more compact functional blanket on the steel surface by adsorption.

In SAD there is a –OH group to form the intramolecular hydrogen bonding but no aryl group for intermolecular assembly. In BAD these two molecular requirements are absent. Hence the supramolecular assembly is not possible in BAD and SAD and show lower efficiency than SATD.

CONCLUSION

- The synthesized benzodiazepine derivatives are good corrosion inhibitor for mild steel in sulphuric acid medium and act by adsorption
- The adsorption of the compounds obey Langmuir adsorption isotherm.
- Electrochemical study shows that they are mixed type inhibitors.
- SEM studies confirmed the formation of a protective film of the inhibitor on the mild steel surface.
- The inhibition efficiency obtained by experimental methods is consistent with the results obtained through theoretical calculations.

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