STUDY OF CORROSION INHIBITION PROPERTIES OF NOVEL SEMICARBAZONES ON MILD STEEL IN ACIDIC SOLUTIONS

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ABSTRACT

The inhibition efficiency of corrosion on mild steel using acids by three different novel Semicarbazones as inhibitors have been studied using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The inhibition efficiency, corrosion rate, the nature of anchoring sites and the adsorption characteristics have been determined from the results. It was found that the newly synthesized compounds behaved as mixed type inhibitors with high inhibition efficiency. The inhibition efficiency increases with increasing the inhibitors concentration but decreases with increasing the temperature. Addition of halide ion enhances the inhibition efficiency. The adsorption of the inhibitors on the mild steel surface obey Langmuir adsorption isotherm. Scanning Electron Spectroscopy is used to examine the surface morphology of mild steel samples both in the presence and absence of inhibitors at optimum conditions. Scanning Electron Microscope reveals the formation of a smooth, dense protective layer in the presence of inhibitor.

Key words: Acid solutions; mild steel; 2, 6-diphenylpiperidin-4-one semicarbazones; potentiodynamic Polarisation; Inhibitor; electro chemical impedance; Scanning Electron Spectroscopy

INTRODUCTION

Corrosion is the primary means by which metals deteriorate. Most metals corrode in contact with water and also moisture in the air, acids, bases, salts, aggressive metal polishes and other corrosive solids and liquid chemicals. A suitable, effective and economical method has to be adopted depending upon the metal and its environment. Mild steel is of high industrial value. Metals, when subjected to surface treatment such as painting, enameling etc. should have clean surface, free from rust or oxide scales. For removing these rusts and scales, metals are immersed in acid solutions known as acid pickling bath. Generally hydrochloric acid is used in pickling bath. However, now-a-days sulphuric acid has replaced hydrochloric acid as pickling solution due to its economic advantage. Soon after the scales are removed, the acids may attack the metal. To prevent this attack, corrosion inhibitors are generally added to acid solutions. A thorough survey of literature reveals that large number of inorganic and organic compounds have been synthesized and employed as corrosion inhibitors ¹⁻⁶. The survey suggests that mild steel corrosion is effectively controlled by the use of organic substances containing nitrogen, oxygen or sulphur in the conjugated system ⁷⁻⁹.

In the pursuit of a suitable inhibitor for the corrosion of mild steel it was proposed to use 2, 6-diphenylpiperidin-4-one semicarbazone and its derivatives for the present work. Their influences on the corrosion of mild steel have also been investigated.

MATERIAL AND METHODS

Experimental

Mild steel specimens of size 5cm × 2 cm × 0.05cm have been used for weight loss method. Mild steel specimens of same composition with an exposed area of 1sq.cm were used for potentiodynamic polarization and AC impedance measurements.

All the three additives (S1, S2 and S3) were preliminarily screened by weight loss method. The metal specimens were initially weighed prior to immersion in 1M H₂SO₄ and 1M HCl as corrodant. After a period of 1 hour, the specimens were removed, washed with water, dried and weighed to an accuracy of four decimals. From the initial and final masses of the specimen (before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various inhibitor concentrations (0.5mM-8mM) in 1M H₂SO₄, 1M HCl and 0.5M H₂SO₄.

To study the effect of temperature the above procedure was carried out at different temperature ranges 40°C-60°C using thermostat. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit (ACM Gill instrument model 903). A platinum foil and Hg | HgSO₄ | 1N H₂SO₄ electrode were used as auxiliary and reference electrode, respectively. Double layer capacitance and charge transfer resistance value were obtained using AC impedance measurements.

Synthesis of Inhibitors

Synthesis of *r*-2, *c*-6-diphenylpiperidin-4-one semicarbazone(S1)

The method of Balasubramaniam and Padma ¹⁰ was followed for the preparation of the compound *r*-2, *c*-6-diphenylpiperidin-4-one (P1). To the solution of

r-2, *c*-6-diphenylpiperidin-4-one (1.2g in 15 ml ethanol), ethanolic solution of semicarbazide hydrochloride (0.5g) and sodium acetate (0.5g) were added. The resulting mixture was stirred by use of magnetic stirrer till the precipitate was formed. The product formed was filtered off and washed with water. Crystallization from ethanol gave 62% yield with an m.pt range of 176-178°C

Synthesis of *r*-2, *c*-6-diphenyl-*t*-3-ethylpiperidin-4-one semicarbazone (S2)

Preparation of *r*-2, *c*-6-diphenyl-*t*-3-ethylpiperidin-4-one (P2) was prepared according to the procedure of Noller and Baliah ¹¹. Ethanolic solution of semicarbazide hydrochloride (0.5g) and sodium acetate (0.5g) were added to *r*-2, *c*-6-diphenyl-*t*-3-ethylpiperidin-4-one (1.5g in ethanol). The contents of the flask were shaken well for 15 minutes and kept at room temperature overnight. The product formed was filtered, washed and recrystallised from ethanol with yield 52% and m.pt range 184-186°C

Synthesis of *r*-2, *c*-6-diphenyl-*t*-3-isopropylpiperidin-4-one semicarbazone (S3)

The procedure given by Noller and Baliah ¹¹ was followed for the synthesis of *r*-2, *c*-6-diphenyl-*t*-3-isopropylpiperidin-4-one. The method used for the synthesis of S2 is adopted for the synthesis of S3 with yield 56% and m.pt 191-193°C

CORROSION MONITORING TECHNIQUES USED

There are basically two general class of corrosion monitoring techniques. They are physico chemical methods and electro chemical methods.

Physicochemical method

Weight loss method or coupon method

In this method, the loss of metal due to corrosion is measured by exposing the metal specimen of known area to the environment for a period of time and the difference in weight before and after exposure is calculated.

Experimental procedure

The initial weight of the polished plate was taken. The solutions were taken in a 100 ml beaker and the specimens were suspended in duplicate into the solution using glass hooks. After a period of one hour, the specimens were removed, washed with water, dried and weighed to an accuracy of four decimals. From the initial and final masses of the specimen (before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various inhibitor concentrations in 1N H₂SO₄, 0.5N H₂SO₄ and 1N HCl. The procedure was repeated for various concentrations of the all the inhibitors prepared.

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The corrosion rate in mmpy is calculated as follows,

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{weight loss (mg)}}{\text{Density (g/cc)} \times \text{area (cm}^2\text{)} \times \text{time (hrs)}}$$

$$1\text{ mpy} = 0.0254 \text{ mm/y}$$

Evaluation of efficiency of inhibitor

Inhibitor efficiency has been determined by using the following relationship

$$I.E(\%) = \frac{W_o - W_i}{W_i} \times 100$$

Where W_o is the weight loss without inhibitor and W_i is the weight loss with inhibitor.

Evaluation of surface coverage (θ)

$$\text{surface coverage}(\theta) = \frac{W_b - W_i}{W_b} \times 100$$

Where W_b and W_i are the weight losses per unit time without and with inhibitor respectively. From this a graph was drawn between C/θ Vs C or C/θ Vs $\log C$ to know whether the adsorption of inhibitor, follows Temkin's / Langmuir isotherm to obtain a linear relationship.

ELECTRO CHEMICAL METHODS

Galvanostatic or Galvanodynamic test

Galvanostatic test are conducted with the controlled current instrument. The current is increased at regular intervals or continuously and the resulting specimen potential is measured. This can be done after it has reached a steady state value or it is plotted automatically. This technique is applied for both anodic and cathodic polarization measurements. At about 50 mV from open circuit potential, curves exhibit linear behavior in accordance with the Tafel equation for polarization under activation control.

$$\eta = \varphi \pm a \ln i / i_0$$

Where φ - the over voltage, i - applied current, i_0 - the exchange current density at the reversible potential.

Potentiodynamic or potentiostatic polarization method

Experimentally, the polarization characteristic is measured by plotting the current response as a function of the applied potential. Usually log current function is plotted against potential on a semi log chart. In order to measure and control the potential and current flow of a corroding metal specimen, it is necessary to use a three electrode system via specimen or working electrode, auxiliary electrode and a reference electrode. A typical standard polarization test cell recommended by ASTM-GS could be used for taking the electrolyte and mounting the electrodes. After connecting the electrodes with proper instrument, the potential of the corroding specimen can be changed stepwise at regular intervals or changed continuously at a constant scan rate at fixed temperature¹⁷. The current that results for each change in potential is recorded. The corrosion rate can be calculated from the following equation,

$$\text{Corrosion rate (mmpy)} = \frac{0.13 \times i_{\text{corr}} \times E.W}{d}$$

where i_{corr} = corrosion current density in mA cm².
E.W = equivalent weight of corroding specimen in gm.
d = density of the metal in g/cm³.

Tafel Polarization Method

In this method a plot of E Vs $\log i$ is made at high over potentials. The rate expression is

$$i = \frac{i_{\text{corr}} [\exp 2.3(E - E_{\text{corr}})]}{\beta_c}$$

Taking log on both sides

$$\log i = \frac{\log i_{\text{corr}} + (E - E_{\text{corr}})]}{\beta_c}$$

The plot of E Vs $\log i$ gives a straight line with slope β_c and the intercept give i_{corr} . From i_{corr} values, the corrosion rate in mmpy obtained by using the relationship

$$\text{Corrosion rate} = \frac{3.2 \times i_{\text{corr}} (\text{mA/cm}^2)}{d} \times \text{Eq. Wt}$$

Linear Polarization Method

Stem and Geary have shown that there is a linear relationship between current and potential when $\eta = 20\text{mV}$ and on measuring the slope of η plot, the corrosion current can be obtained by using the following equation.

$$i_{\text{corr}} = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)} \times \frac{1}{dn/di}$$

(Anodic and cathodic reaction activation controlled)

(Anodic reaction activation controlled and cathodic reaction diffusion controlled)

$$i_{\text{corr}} = \frac{\beta_a}{dn/di}$$

The term dn/di has the dimension of resistance. Hence this method is also known as polarization resistance method.

β_a - Anodic Tafel slope

β_c - cathodic Tafel slope

The i_{corr} is calculated from the above relationship. The value of β_a and β_c are obtained from the slopes of the plots of η Vs $\log i$.

A.C. Impedance Methods

Alternating current (AC) techniques can provide additional information. Specifically, electrode surface possess an excess surface charge which is balanced by anion accumulation of opposite sign in the adjacent solution, thus making the system electrically neutral. The existence of such a double layer near the electrode surface makes the electrode equivalent to a conventional capacitor and this is the basis of A.C. method..

Corrosion Rate

After calculating R_i from Nyquist plot and substituting Tafel slope values for cathodic β_c and anodic β_a in the equation.

$$i_{\text{corr}} = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)} \times 1/R_t$$

$$IE(\%) = \frac{i_{\text{corr}}(o) - i_{\text{corr}}(\text{inh})}{i_{\text{corr}}(o)} \times 100$$

$i_{\text{corr}}(o)$ and $i_{\text{corr}}(\text{inh})$ are corrosion current density values in the absence and presence of inhibitors respectively²⁰.

The corrosion current density of the particular system can be calculated. Thus without disturbing the system much, the corrosion rate can be accurately calculated by A.C. impedance method.

Electrode preparation

Mild steel specimens of size (5cm × 2 cm × 0.05cm) were used. The plates were washed, dried and polished successively using emery sheets of extra coarse, coarse, medium, fine and extra fine grades to remove adhering impurities finally degreased with acetone and dried using a drier. The plates were then kept in a desiccator to avoid the absorption of moisture by the plates.

Calculations

Potentiodynamic polarization technique (Tafel polarization method)

Polarization studies were carried out for mild steel to evaluate the corrosion kinetic parameters such as i_{corr} , E_{corr} and Tafel slopes β_a & β_c .

Electrode

The mild steel electrodes used for the polarization studies have the same composition as that used for weight loss studies. Cylinders of the mild steel having diameter 1mm were embedded in a Teflon holder with an exposed area of 1 sq.cm were used for the present study.

Electrode surface preparation

The mild steel electrode was first cleaned with acid, washed with distilled water and dried. The surface of the electrode was first polished successfully with emery papers. It was then rinsed with distilled water and degreased with acetone. It was thoroughly dried and immediately used for polarization studies.

Electrode cell assembly

The polarization studies were carried out using standard polarization test cells. It consisted of a glass beaker covered with a four hold Teflon top. The biggest hole was used for fitting the mild steel electrode. The smaller hole was used for fitting the reference electrode through lugg-in. The smallest hole was used for fitting the counter electrode. One more hole was provided for purging the inert gas, if needed. The mild steel electrode was then placed in the test solution (uninhibited & inhibited solutions of 3 different concentrations) for 20-30 minutes before electrochemical measurements.

Electrochemical study

Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit (ACM Gill instrument, model 903). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01Hz with single amplitude of 10mV. The Tafel polarization measurements were made after EIS studies for a potential range of -200 mV to +200mV with respect to open circuit potential, at a scan rate of 1mV per sec. the I_{corr} , E_{corr} , R_t and C_{dl} values were obtained from the data using the corresponding Corr view and Z view software's.

The synergistic effect was studied by the addition of 1mM KI and 1mM H_2SO_4 containing various concentration of the inhibitors S1, S2 and S3 for the duration of 1 hour. From the weight loss the corrosion rate and inhibition efficiency was calculated.

RESULTS AND DISCUSSIONS

The synthesized compounds (Fig.1) were characterized by elemental analysis (Table 1), IR, NMR and ^{13}C NMR spectral studies. Analysis of the IR spectra of the compounds S1, S2 and S3 indicates that all the compounds show two strong bands in the regions 3525-3398 cm^{-1} and 3400-3367 cm^{-1} assignable to ν_{asym} (N-H) and ν_{sym} (N-H), respectively of the $-NH_2$ group of the compounds^{12,13}. Another medium intensity broad band around 3319-3306 cm^{-1} found in the IR spectra of these compounds is due to $-NH$ stretching vibration involving ring nitrogen. Bands appearing in the region 3100-3030 cm^{-1} , 2975-2950 cm^{-1} and 2898-2850 cm^{-1} are due to aromatic ν (C-H), aliphatic and alicyclic ν_{asym} (C-H) and aliphatic and alicyclic ν_{sym} (C-H) respectively. A medium to sharp band observed in the region 1568-1492 cm^{-1} is attributed to ν (C=N) stretching¹⁴ which indicate the presence of azomethine group in the compound. A strong band in the region 1720-1680 cm^{-1} is mainly due to C=O stretching mode¹⁵. In addition several other bands in the region 1450-900 cm^{-1} can be attributed to vibrations involving interactions between C=O stretching and C-N stretching (Table 2).

Ligand	R ¹	R ²
(S1)	H	H
(S2)	C ₂ H ₅	H
(S3)	i-C ₃ H ₇	H

Fig 1. Structures of the Compounds S1, S2 & S3.

Fig 2. IR Spectra of the ligand S1.

Table 1. Physical and analytical data of 2,6-diphenylpiperidin-4-one semicarbazones.

S.No	Ligands Molecular Formula	Melting point (°C)	Yield (%)	Elements found (calc)		
				C (%)	H (%)	N (%)
(S ¹)	C ₁₈ H ₂₀ N ₄ O	178-180°	65	70.20 (70.09)	6.29 (6.54)	18.01 (18.18)
(S ²)	C ₂₀ H ₂₄ N ₄ O	190-192°	70	71.22 (71.39)	7.03 (7.19)	16.52 (16.66)
(S ³)	C ₂₁ H ₂₆ N ₄ O	186-188°	65	71.39 (71.96)	7.62 (7.48)	16.04 (15.99)

1H NMR Spectral Studies

The N-H proton of piperidone ring system usually exhibit singlet in the region 2.00-2.07ppm¹⁶. The compound S1 shows a singlet at 2.1ppm is assignable to N-H of piperidin-4-one semicarbazone. All the compounds exhibit a singlet in the region 8.6-8.8ppm is due to =N-NH proton. The $-CONH_2$ group of the compounds give two broad signals ~5.3 and ~6.3ppm. The presence of these broad peaks indicates the two protons are nonequivalent and this may be due to restricted rotation of $-CONH_2$ bond as a result of orientation of semicarbazone group in space. All the compounds show multiplet between 7.24-7.61ppm which is due to aromatic protons (Fig 1b & Table 3).

Fig 3. 1H chemical shift data (ppm) S2.

^{13}C NMR Spectral Studies

The ^{13}C NMR spectral data of the ligands (S1, S2 and S3) are given in the Fig 4 & Table 4. The signals in the range 150-152.5 ppm are assigned to the azomethine carbon (C=N)¹⁷. The signal in the range 126-145 ppm^{18,19} is due to aromatic carbon. The signals of the carbon atom of heterocyclic ring occur in the range 36-69 ppm. Thus, IR, 1H NMR Spectral studies and ^{13}C NMR Spectral studies confirm that the ligands (S1, S2 and S3) exist in chair conformation with alkyl and phenyl groups in equatorial orientation and that they exist in keto form rather than enol form.

Table-2 Important IR absorption bands of compounds S1, S2 and S3.

Compound	ν (C=O)	ν (N ⁴ -H)	ν (N ⁴ H) _{asym}	ν (N ⁴ -H) _{symm}	ν (N ² -H)	ν (C=N)
S1	1724s	3306s	3398m	3367m	3085m	1492m
S2	1682s	3319m	3525s	3406s	3186s	1558s
S3	1680s	3317m	3525s	3408s	3192s	1555s

Table 3: ¹H NMR Chemical shift data (ppm) S1, S2 and S3.

Ligand	H-2	H-3		H-5		H-6	Aromatic protons	Ring N-H	-CONH ₂	=NNH	Other protons
		ax	eq	ax	eq						
(L ¹)	3.31 dd j=12,3	1.93 (dd, J=14,12)	2.52 (b)	2.36-2.42(m)		3.75,dd J=11,3	7.2-7.48 (m,10H)	6.2(b)	5.24 b 6.26 b	8.85(s)	-----
(L ³)	3.64 (J=10)	2.45 (t,J=11)		2.18, (dd,J=11.8)	3.0 (dd,J=13.6, 2.9)	3.9(dd,J=11.4,2.4)	7.24-7.46 (m,10.H)	2.07 (s)	5.34(b) 6.15(b)	8.55 (s)	1.25,1.54 (m,2H, c-3-CH ₂ -CH ₃ 0.88(t,3h, c-3-CH ₂ -CH ₃)
(L ⁴)	3.37 d,j=3,10	2.39 (d,j=11)		2.06(dd, J=14.9, 11.5)	3.04(dd, J=11.5,3.2)	3.86 (dd,J=11.1.7)	7.28-7.44 (m,10H)	2.03 (s)	5.42 (b),6.1 (b)	8.77 (s)	1.7(m,c-3 - c-3-CH ₂ -CH ₃ 0.97-1.02 - (2CH ₃)

Fig 4 ¹³C NMR Chemical shift data (ppm) S3**Table 4:** ¹³C NMR Chemical shift data (ppm) S1, S2 and S3.

Ligands	C-2	C-3	C-4	C-5	C-6	-CH ₃	-CH ₂	-CH	-(C=O)	Aromatic carbons
(S1)	69.2	44.6	152.1	36.4	60.4	-----	----	----	158.4	127.2,127.5,127.8, 143.9,144.6
(S2)	67.4	51.3	150.8	36.3	60.5	12.5	19.3	----	158.3	126.6,127.3,127.4, 128.5,128.6,143.8,144.6
(S3)	64.6	54.5	150.6	36.6	59.1	19.3	----	21.3	158.1	127.2,127.5,127.7,128.4, 128.6,128.7,144.7,144.9

Weight loss studies

The tested piperidin-4-one semicarbazones inhibited the corrosion of mild steel even at low concentration of the acid (1M H₂SO₄) at room temperature. The inhibition efficiency was found to increase with increasing inhibitor concentration. The maximum efficiency of about 88-96% was obtained at concentrations of 5mM-8mM of inhibitors (Tables 5) and is depicted in Fig.5

It is observed that all the three compounds inhibit the corrosion of mild steel at all concentrations used in this study. A plot of weight loss versus inhibitor concentration (Fig. 6) reveals that the metal loss and corrosion rate (mpy) progressively decreased with increasing inhibitor concentration as is evident from Table 5

Table 5: Inhibition efficiencies, corrosion rate, Degree of coverage of various concentrations of inhibitors (S1, S2 & S3) for the corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurements at room temperature.

Name of the inhibitor	Inhibitor Concen. (mM)	Weight Loss (gms)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Degree of Coverage
S1	Blank	0.1375		18826.5	
	0.5	0.0245	82.18	3354.54	0.8218
	1	0.0167	87.85	2286.56	0.8785
	2	0.0121	91.2	1656.73	0.9120
	3	0.0089	93.52	1218.58	0.9352
	5	0.0071	94.83	972.13	0.9483
	7	0.0053	96.14	725.67	0.9614
S2	Blank	0.1463		20,031.39	
	0.5	0.0472	67.73	6462.62	0.6773
	1	0.0408	72.11	5586.33	0.7211
	2	0.0313	78.6	4285.59	0.7860
	3	0.0353	75.8	4833.27	0.7580
	5	0.0164	88.79	2245.48	0.8879
	7	0.0195	86.67	2669.94	0.8667
	8	0.0184	87.23	2519.32	0.8723
S3	Blank	0.1413		19,346.79	
	0.5	0.0725	48.69	9926.70	0.4869
	1	0.052	63.19	7119.84	0.6319
	2	0.0414	70.70	5668.48	0.7070
	3	0.0345	75.58	4723.74	0.7558
	5	0.0258	81.74	3532.53	0.8174
	7	0.0127	91.01	1738.88	0.9101
	8	0.0125	91.15	1711.50	0.9115
	9	0.01	92.92	1369.20	0.9292

Fig. 5. Variation of inhibition efficiency with concentration of inhibitors at room temperature in 1M H_2SO_4 **Fig. 6** Plot of Weight loss (gms) Vs concentration (mM) for Inhibition of corrosion of mild steel in 1M H_2SO_4

The corrosion rate in 1M H_2SO_4 for various concentrations of the inhibitors (S1, S2 and S3) was determined after 1 hour of immersion. The corrosion rate expressed in mpy decreased with increasing inhibitor concentration as evident from Tables 5 and fig (7).

Fig. 7. Variation of Corrosion rate as function of concentration of inhibitors for the corrosion of mild steel in 1M H_2SO_4

Adsorption isotherm

The surface coverage (θ) for different inhibitor concentrations was calculated. The observation of Fig. 8, a plot of C/θ versus C gives a straight line confirming that all the three inhibitors obeyed Langmuir adsorption isotherm. This result supports the conclusion that maximum inhibition corresponds to the formation of an adsorbed layer of the inhibitor on the active sites of the metal surface.

Fig. 8. Langmuir's Plot of inhibitors in 1M H_2SO_4

Influence of Temperature

It is evident from Table 6 that in 1M H_2SO_4 the dissolution of the metal increases with rise in temperature both in presence and absence of inhibitor. The efficiency of inhibitor decreases with increase in temperature indicating weak adsorption¹⁹. The decrease in inhibition efficiency with temperature indicates the fact that the inhibitor film formed on the metal surface is less protective in nature at higher temperature²⁰.

Table-6 Inhibition efficiencies of 7mM concentrations of inhibitor (S1,S2 and S3) for the corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurements at higher temperatures.

	Temperature °C	Inhibitor Concentration mM	Weight Loss (gms)	Inhibition Efficiency (%)	Corrosion Rate (mpy)
S1	40	Blank	0.4085		55931.82
		7	0.0101	97.52	1382.89
	50	Blank	0.6758		92530.53
		7	0.0258	96.18	3532.53
	60	Blank	0.9455		129457.86
		7	0.1067	88.71	14609.36
S2	40	Blank	0.4706		64434.55
		5	0.0913	80.59	12500.79
	50	Blank	0.7216		98801.47
		5	0.1755	75.67	24029.46
	60	Blank	1.0530		144176.76
		5	0.3412	67.59	46717.10
S3	40	Blank	0.4151		56835.49
		7	0.0388	90.65	5312.49
	50	Blank	0.6677		91421.48
		7	0.088	86.82	12048.90
	60	Blank	0.8711		119271.01
		7	0.1547	82.24	21181.52

Activation energy (E_a) and free energy of adsorption (ΔG^0_{ads}):

The values of activation energy (E_a) were calculated from the plot of log (corrosion rate) Vs $1000/T$. Fig. 9

$$E_a = \text{slope} \times 8.314 \times 2.303(J)$$

The free energy of adsorption (ΔG^0_{ads}) at various temperatures were calculated using the following equation

$$\Delta G^0_{ads} = -Rt \ln(5.55K)$$

and the equilibrium constant K is given by

$$K = \theta / C(1 - \theta)$$

Where θ is the degree of coverage on the metal surface, C is the concentration of inhibitor in mM

The values of E_a and ΔG^0_{ads} are given in Table 7. The less negative values of ΔG^0_{ads} with increase in temperature indicate the physical adsorption of the inhibitors on the metal surface²¹. The values of E_a in the inhibited acid solution are appreciably greater than those obtained in the uninhibited acid solution. This suggests that the presence of reactive centers on the inhibitors, block the active sites of corrosion resulting in an increasing in activation energy²². This also indicates that these types of indicators are more effective at room temperature, compared to that of higher temperatures²³.

Table 7. Activation energies (E_a) and free energies of adsorption (ΔG^0_{ads}) for the corrosion of mild steel for selected concentrations of the inhibitors in 1M H_2SO_4 .

Name of the inhibitors	E_a 40°C-60°C KJ	ΔG^0_{ads} at various temperature (KJ)		
		40°C	50°C	60°C
Blank	38.29	-	-	-
S1	76.58	-14.943	-14.2231	-11.4393
S2	76.58	-9.9678	-9.4512	-8.6980
S3	57.44	-11.2993	-10.6223	-9.9755

Fig. 9. Arrhenius plot of corrosion rate of mild steel in 1M H_2SO_4 solution in the presence and absence of inhibitor

Electrochemical Studies**A.C Impedance measurements and potentiodynamic polarisation studies**

A.C Impedance measurements were carried out at room temperature for corrosion of mild steel in 1M H_2SO_4 after immersion for about half an hour. The Nyquist plots for mild steel in uninhibited acid and for the three concentrations of the inhibitors (S1, S2 and S3) as are shown in Fig.11-13 and the data have been tabulated (Table 8). Electrochemical impedance spectroscopy analyses provide insight into the kinetics of electrode processes as well as the surface characteristics of the electrochemical system of interest. The observed increase in the impedance parameters in inhibited solutions is associated with the corrosion inhibiting effect of the inhibitors S1, S2 and S3. The Nyquist plots for all systems generally have the form of only one

depressed semicircle, corresponding to one time constant, although a slight sign of low-frequency inductive behaviour can be discerned. The depression of the capacitance semicircle with centre below the real axis suggests a distribution of the capacitance due to inhomogeneities associated with the electrode surface. The Rct, value can be extracted from the diameter of the semicircle. The impedance spectra for the Nyquist plots were thus adequately analyzed by being fit to the equivalent circuit model $R_s(C_{dl} R_{ct})$, which has been previously used to model the mild steel/acid solution interface. Introduction of inhibitors S1, S2, & S3 into the acid corrodent leads to an increase in Rct and a reduction of Cdl, indicating a hindering of the corrosion reaction. The decrease in Cdl values, which normally results from a decrease in the dielectric constant and/or an increase in the double layer thickness, is due to inhibitor adsorption on the metal/electrolyte interface. This implies that the inhibitors reduce the corrosion rate of the mild steel specimen by virtue of adsorption on the metal/electrolyte interface, a fact that has been previously established. A quantitative measure of the protective effect can be obtained by comparing the values of the charge transfer resistance in the absence (Rct) and presence of (Rctinh) inhibitor as follows:

$$IE(\%) = \left[1 - \frac{R_{ct}}{R_{ctinh}} \right] \times 100$$

Where Rct and Rctinh are the charge transfer resistance for inhibited and uninhibited systems, respectively. The values of charge transfer resistance are calculated by the difference of impedance at high and low frequencies on the real axis, as suggested by Haruyama and Tsuru²⁴. The capacity C is determined at the frequency for which the imaginary part of the impedance is maximum ($-Z^{max}_{imag}$) from the equation:

$$f(-Z^{max}_{imag}) = \frac{1}{2\pi C_{dl} R_{ct}}$$

The double layer capacitance values of the systems were also examined and calculated using the expression:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

Low double layer capacitance suggests reduced electric charge stored, which is a consequence of increased adsorption layer that acted as a dielectric constant. The increase in values in inhibited systems which corresponds to an increase in the diameter of the Nyquist semicircle confirms that the corrosion inhibiting effect of S1, S2 & S3 and inhibitors + KI and is much more pronounced in the latter system, implying that KI synergistically enhanced the corrosion inhibiting effect of inhibitors of S1, S2 & S3.

The Simplified Randles cell is one of most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer (or polarization resistance). The double-layer capacitance is in parallel with the charge-transfer resistance. In addition to being a useful model in its own right, the Simplified Randles Cell is the starting point for other more complex models. The equivalent circuit for a Simplified Randles Cell is shown in Figure 10.

Fig. 10 The suggested equivalent circuit model for the studied system.

The charge transfer resistance (R_t) value for mild steel in uninhibited H_2SO_4 significantly changes after the addition of inhibitor. The value of charge transfer resistance increases with increase in concentration. The fact is advocated by the increase in inhibitor efficiency.

The semicircular nature of Nyquist plots obtained from all experiments indicates that corrosion of mild steel is controlled by charge transfer process as shown in Fig. (11-13).

The double Layer Capacitance (C_{dl}) decreases with increasing inhibitor concentration. The decrease in C_{dl} values in presence of inhibitors indicated the fact that these additives inhibit corrosion by adsorption on the metal surface^{25, 26}.

The various corrosion kinetic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c) were derived from potentiodynamic polarization studies on mild steel in 1M H_2SO_4 , both in the presence and absence of inhibitors S1, S2 and S3 at different

concentrations, Table-9, the polarization curves are depicted in Fig. (14-16). The E_{corr} values are shifted slightly in the presence of the inhibitors. The I_{corr} value decreases with the addition of inhibitor. Tafel slopes β_a and β_c are affected to the same extent by the addition of inhibitors (S1, S2 and S3), indicating that the inhibitors act as mixed type inhibitors.

It is observed that the results of surface coverage in presence of inhibitors (S1, S2 and S3) are in good agreement with those given by weight loss technique. This means that the inhibition efficiency calculated with the help of galvanostatic polarisation technique are nearly equal to the values obtained by weight loss technique.

Table 8 A.C-Impedance parameters for corrosion of mild steel in 1M H_2SO_4 for the selected concentrations of inhibitors (S1, S2 & S3)

Name of the inhibitors	Inhibitors concentration mM	R_{ct} Ohm cm^2	C_{dl} F	Inhibition Efficiency (%)
S1	Blank	2.690	2.905×10^{-4}	
	2	10.92	8.265×10^{-5}	81.98
	5	19.79	7.432×10^{-5}	91.00
	7	30.56	5.171×10^{-5}	92.45
S2	Blank	2.690	2.905×10^{-4}	
	2	14.93	1.595×10^{-4}	75.36
	5	29.89	9.038×10^{-5}	86.40
	8	35.62	9.959×10^{-5}	91.19
S3	Blank	2.690	2.905×10^{-4}	
	2	12.88	9.496×10^{-5}	79.11
	3	27.76	8.698×10^{-5}	90.31
	5	28.86	6.892×10^{-5}	90.68

Table-9 Corrosion parameters for corrosion of mild steel in 1 MH_2SO_4 by potentiodynamic polarization method]

Name of the inhibitors	Inhibitor concentration mM	Tafel slopes mV/decade		E_{corr} mV	I_{corr} mA/cm ²	Inhibitor Efficiency %
		β_a	β_c			
S1	Blank	37.0766	73.2076	-472	1.34859	
	2	40.3469	81.1849	-481	0.01495	47.05
	5	80.0441	99.4557	-483	0.7140	98.89
	7	26.086	69.7466	-469	0.2662	80.25
S2	Blank	37.0766	73.2076	-472	1.34859	
	2	46.3751	93.0977	-479	0.89812	33.403
	5	42.5960	88.2886	-482	0.5847	56.64
	8	26.2288	79.4684	-471	0.3401	74.78
S3	Blank	37.0766	73.2076	-472	1.34859	
	2	53.1887	101.600	-485	0.7868	41.65
	3	20.740	69.7164	-464	0.2515	81.35
	5	34.1767	112.062	-483	0.3988	70.43

Fig . 11 Nyquist diagrams for mild steel in 1M H_2SO_4 for selected concentration of S1
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S1 3) 1M H_2SO_4 + 5mM S1 4) 1M H_2SO_4 + 7mM S1

Fig. 12 Nyquist diagrams for mild steel in 1M H_2SO_4 for selected concentration of S2
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S2 3) 1M H_2SO_4 + 5mM S2 4) 1M H_2SO_4 + 8mM S2

Fig . 13 Nyquist diagrams for mild steel in 1M H_2SO_4 for selected concentration of S3
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S3 3) 1M H_2SO_4 + 3mM S3 4) 1M H_2SO_4 + 5mM S3

Fig .14 Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S1
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S1 3) 1M H_2SO_4 + 5mM S1 4) 1M H_2SO_4 + 7mM S1

Fig 15 Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S2
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S2 3) 1M H_2SO_4 + 5mM S2 4) 1M H_2SO_4 + 8mM S2

Fig . 16 Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S3
1) 1M H_2SO_4 2) 1M H_2SO_4 + 2mM S3 3) 1M H_2SO_4 + 3mM S3 4) 1M H_2SO_4 + 5mM S3

Synergistic effect

A comparative study of synergistic effect of corrosion on mild steel in 1M H_2SO_4 by a combination of inhibitors S1, S2 & S3 with and without addition of iodide ions have been studied by weight loss method. The results are given in Table 10 and corrosion inhibition is found to increase with increase in concentration of inhibitors S1, S2 and S3. It is evident from the Tables that iodide ions enhance the inhibition of the three inhibitors^{27, 28}. When I^- ions are added to the inhibiting solution, they are chemisorbed by forming chemical bonds on the positively charged steel surface in 1M H_2SO_4 . This strong chemisorptions of I^- ion shifts the metal to a more positive potential and enhances inhibitor property. The cooperative effect between S1, S2 & S3 and KI in hindering the corrosion of mild steel in 1.0M H_2SO_4 solution is also evident in both the Nyquist and Tafel polarization plots. Addition of KI resulted in a significant increase in the diameter of the Nyquist semicircle and hence an increase in as well as and a decrease in the corrosion current density of the Tafel polarization curves. The presence of iodide ions shifts more in the cathodic direction and further decreases the anodic and cathodic reaction kinetics. The mechanism of this synergistic effect has been described in detail in some reports. The iodide ions are strongly chemisorbed on the corroding mild steel surface and facilitate S1, S2 & S3 adsorption by acting as intermediate bridges between the positively charged metal surface and inhibitor. This stabilizes the adsorption of S1, S2 & S3 on the mild steel surface, leading to higher surface coverage. To account for the above observations, it is necessary to recognize that the process of adsorption of an organic inhibitor on a corroding metal surface depends on factors such as the nature and surface charge on the metal in the corrosive medium as well as the inhibitor structure. Consequently, more iodide ions are adsorbed on mild steel which presents a more positive surface, giving rise to increased synergistic interactions and hence higher inhibition efficiencies.

Table-10 Synergistic effect of 1mM KI on the inhibition efficiency of S1, S2 and S3 by weight loss method at room temperature.

Name of the inhibitor	Inhibitor Concn. (mM)	Inhibitor efficiency (%)	
		Without KI	With 1mM KI
S1	0.5	82.18	91.39
	1	87.85	96.93
	2	91.2	98.88
	3	93.52	99.17
	5	94.83	99.42
	7	96.14	99.83
S2	0.5	67.73	72.85
	1	72.11	85.07
	2	78.6	90.76
	3	75.8	94.7
	5	88.79	97.66
	7	86.67	97.76
S3	0.5	48.69	68.52
	1	63.19	86.69
	2	70.70	93.16
	3	75.58	95.05

Inhibiting efficiency of the inhibitors in 1M HCl and 0.5M H_2SO_4

Weight loss studies were carried out with various concentrations of inhibitors S1, S2 and S3 in 1MHCl (Table 11) and 0.5M H_2SO_4 . It is found that inhibition efficiency is maximum in 0.5M H_2SO_4 compared with 1MHCl, for all concentration of inhibitors as is evident from Table 12. All the compounds inhibit corrosion by adsorption mechanism and adsorption of these compounds follow Langmuir's adsorption isotherm in 1M HCl (Fig.17). Variations of inhibition efficiency, weight loss and corrosion rate with concentration were depicted in (Figs.18-20) in 1M HCl.

Table-11 Inhibition efficiency of inhibitor S1, S2 and S3 in 1M HCl and 0.5M H_2SO_4

Inhibitor	Inhibitor Concn. (mM)	Inhibitor efficiency (%)	
		0.5M H_2SO_4	1M HCl
S1	0.5	73.74	68.75
	1	83.94	76.38
	2	88.00	82.29
	3	91.02	84.37
	5	93.29	90.62
S2	0.5	63.34	58.76
	1	74.30	61.10
	2	80.47	65.87
	3	85.85	75.35
	5	88.24	86.25
	7	91.93	72.51
S3	0.5	58.17	47.73
	1	66.02	67.83
	2	88.75	78.64

Fig. 17 Langmuir's Plot of inhibitors in 1M HCl

Fig. 18 variation of corrosion rate as an function of concentration of inhibitors for the corrosion of mild steel in 1M HCl.

Fig. 19 Variation of inhibitor efficiency with concentration of inhibitors at room temperature in 1M HCl

Fig. 20 Plot of Weight loss (gms) Vs concentration (mM) for Inhibition of corrosion of mild steel in 1M HCl

Table-12 Inhibition efficiencies of various concentrations of inhibitor S1,S2 and S3 for the corrosion of mild steel in 1M HCl obtained by weight loss measurements at room temperature

Name of the inhibitor	Inhibitor Concn. (mM)	Weight Loss (gms)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Degree of Coverage
S1	Blank	0.0288		3943.2	
	0.5	0.009	68.75	1232.2	0.6875
	1	0.0068	76.38	931.05	0.7638
	2	0.0051	82.29	698.29	0.8229
	3	0.0045	84.37	616.14	0.8437
	5	0.0027	90.62	369.68	0.9062
S2	Blank	0.0211		2889.01	
	0.5	0.0087	58.76	1191.20	0.5876
	1	0.0082	61.1	1122.74	0.6100
	2	0.0072	65.87	985.82	0.6587
	3	0.0052	75.35	711.98	0.7535
	5	0.0029	86.25	397.06	0.9241
	7	0.0058	72.51	794.13	0.7251
	8	0.0059	72.03	807.82	0.7203
S3	Blank	0.0398		5449.4	
	0.5	0.0208	47.73	2847.93	0.4773
	1	0.0128	67.83	1752.57	0.6783
	2	0.0087	78.64	1163.82	0.7864
	3	0.005	87.43	684.6	0.8743
	5	0.003	92.46	410.76	0.9246
	7	0.0045	88.69	616.14	0.8869

Scanning Electron Microscope (SEM)

Surface of polished mild steel specimens immersed in 1M H_2SO_4 in the presence and absence of inhibitor S1 was examined using SEM. When a blank determination was conducted, the metal's surface was corroded with etched grain boundaries and other corrosion products were also noticed as seen in

the Fig.21. The micrograph reveals that the surface is strongly damaged in the absence of inhibitor (active corrosion). But in the presence of inhibitors, the micrograph reveals that there is decrease in the corrosion sites and pits over the surface of the mild steel (Fig.22). This is due to the formation of adsorption layer of inhibitor on the metal surface.

Fig. 21 scanning electron micrograph of mild steel sample after immersion in 1M H₂SO₄

Fig. 22 Scanning electron micrograph of mild steel sample after immersion in 1M H₂SO₄ in presence of ppm of inhibitors.

From these observations we can say that the inhibitor gives a good inhibition effect for the mild steel and thus confirms the results obtained from other techniques.

CONCLUSION

The extent of these adsorption of different inhibitors at a fixed concentration would depend upon, the surface area of the inhibitor molecules, the number of active centers such as N,S,O atoms and the intensities of lone pairs of electrons on these sites along with the intensities of π electrons on aromatic rings. It is well known that iron has coordinating affinity toward, nitrogen, sulphur and oxygen-bearing ligands. Hence, adsorption on iron can be attributed to coordination through $-\text{NH}-\text{CO}-$ group, $-\text{C}=\text{N}$ and $-\text{NH}_2$ hetero atom (N and O), and π -electrons of aromatic ring.²⁹⁻³³

The percentage inhibition efficiency exhibited by these inhibitors is high and supposed to be due to strong adsorption of the inhibitors on the metal surface thereby preventing corrosion of mild steel in acid solutions. The inhibition efficiency of piperidin-4-one semicarbazones (S1, S2 and S3) are expected to adsorb through the lone pairs of electrons on N and O atoms as well as π electron density on the phenyl ring by their coordination with the metal surface.

The inhibitors Among the compounds investigated in the present study the order of IE has been found as S1 > S2 > S3

The inhibition of active dissolution of the metal is due to the adsorption of the inhibitor molecules on the metal surface forming a protective film. The inhibitor molecules can be adsorbed onto the metal surface through electron transfer from the adsorbed species to the vacant electron orbital of low energy in the metal to form a co-ordinate type link

The three compounds were found to inhibit the corrosion of mild steel in 1M H₂SO₄ and 1M HCl by forming an insoluble protective layer on the surface.

The following conclusions can be drawn on the basis of the present investigation.

- Piperidin -4- one semicarbazones are effective inhibitors for corrosion of mild steel in 1M H₂SO₄ at optimum concentration of (5mM -8mM).
- The inhibition efficiency increases with increasing inhibitor concentration.
- All the compounds inhibit corrosion by adsorption mechanism and adsorption of these compounds from acid solution follow Langmuir's adsorption isotherm.
- Higher values of thermodynamic activation function (Ea) for inhibited system than those for uninhibited acids show the temperature dependence on inhibition efficiency.
- The negative ΔG° values indicate the spontaneous adsorption of the inhibitors on the surface of mild steel.
- Electrochemical impedance spectroscopy experiments have shown that an increase in inhibitor concentration causes an increase in polarization resistance R_p, whereas a decrease in C_{dl} values, is due to the increase in thickness of the adsorbed layer.
- The Tafel slopes obtained from potentiodynamic polarization curves indicate that all the compounds behave as mixed type inhibitors with more cathodic character in 1M H₂SO₄.
- Addition of halide ions enhances inhibition efficiency.
- It can be noted that S1, S2 and S3's inhibition performance is better in H₂SO₄ than in HCl.
- Scanning Electron Microscope reveals the formation of a smooth, dense protective layer in the presence of inhibitor.

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