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Evaluation of novel Semicarbazones as corrosion inhibitors for mild steel in acidic solutions

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ABSTRACT

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.

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 size5cm ×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.

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^{0}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^{0}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 (P3). The method used for the synthesis of S2 is adopted for the synthesis of S3 with yield 56% and m.pt 191-193^{0}C

Techniques used

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 H_2SO_4 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 H_2SO_4, 1M HCl and 0.5M H_2SO_4.

To study the effect of temperature the above procedure was carried out at different temperature ranges 40^{0}C-60^{0}C using thermostat. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical

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measurement unit (ACM Gill instrument model 903). A platinum foil and Hg | $HgSO_4$ |1N H_2SO_4 electrode were used as auxiliary and reference electrode, respectively. Double layer capacitance and charge transfer resistance value were obtained using AC impedance measurements.

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.1a) were characterized by elemental analysis (Table 1), IR, NMR and ^{13}C NMR spectral studies.

IR 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 3525-3398cm^{-1} and 3400-3367cm^{-1} assignable to ν_{asym}(N-H) and ν_{sym} (N-H), respectively of the $–N^4H_2$ group of the compounds[12,13]. Another medium intensity broad band around 3319-3306cm^{-1} found in the IR spectra of these compounds is due to –NH stretching vibration involving ring nitrogen. Bands appearing in the region 3100-3030cm^{-1}, 2975-2950cm^{-1} and 2898-2850cm^{-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 1568-1492cm^{-1} is attributed to ν(C=N) stretching [14] which indicate the presence of azomethine group in the compound. A strong band in the region 1720-1680cm^{-1} is mainly due to C=O stretching mode [15]. In addition several other bands in the region 1450-900cm^{-1} can be attributed to vibrations involving interactions between C=O stretching and C-N stretching (Table 2)

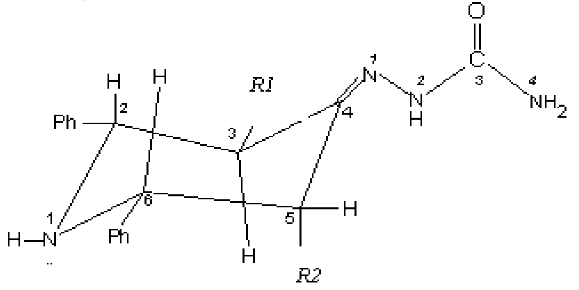


Fig. 1 a Structures of the Ligands

^{1}H NMR Spectral Studies

The N-H proton of piperidone ring system usually exhibit singlet in the region 2.00-2.07ppm [16] 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).

^{13}C NMR Spectral Studies

The ^{13}C NMR spectral data of the ligands (S1, S2 and S3)are given in the Fig 1c &

Table 4.The signals in the range 150-152.5 ppm is 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.

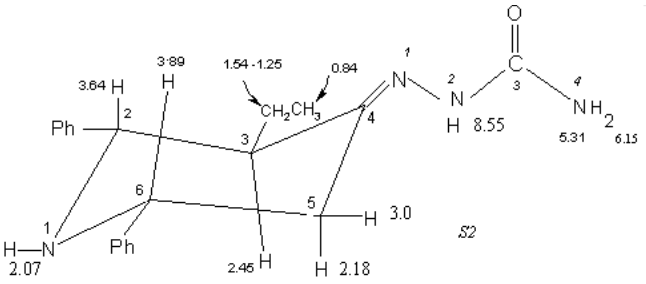


Fig 1b H^{1}chemical shift data(ppm) S2

Thus, IR, ^{1}H NMR Spectral studies and ^{13}C NMR Spectral studies confirm that the ligands (S1, S2 and S3) exist in chair confirmation with alkyl and phenyl groups in equatorial orientation and that they exist in keto form rather than enol form.

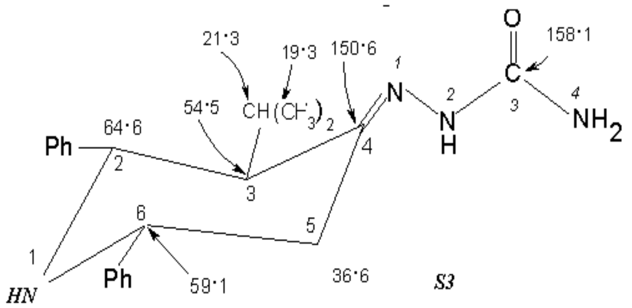


Fig 1c. ^{13}C NMR Chemical shift data (ppm) S3

Weight loss studies

The tested piperidin-4-one semicarbazones inhibited the corrosion of mild steel even at low concentration of the acid (1M H_2SO_4) 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.2. 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. 3) reveals that the metal loss and corrosion rate (mpy) progressively decreased with increasing inhibitor concentration as is evident from Table 5

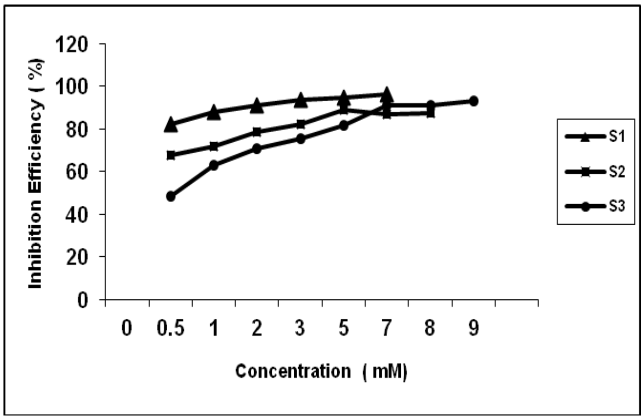


Fig. 2 Variation of inhibition efficiency with concentration of inhibitors at room temperature in 1M H_2SO_4

The corrosion rate in 1M H_2SO_4 for various concentrations of the inhibitors (S1, S2 and S3) was determined after 1hour of immersion. The corrosion rate expressed in mpy decreased with increasing inhibitor concentration as evident from Tables 5 and fig (4).

Adsorption isotherm

The surface coverage (θ) for different inhibitor concentrations was calculated. The observation of Fig. 5, 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.

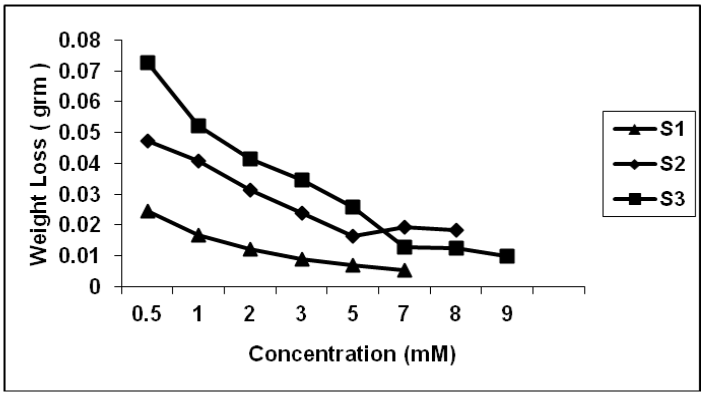


Fig. 3 Plot of Weight loss (gms) Vs concentration (mM) for Inhibition of corrosion of mild steel in 1M H_2SO_4

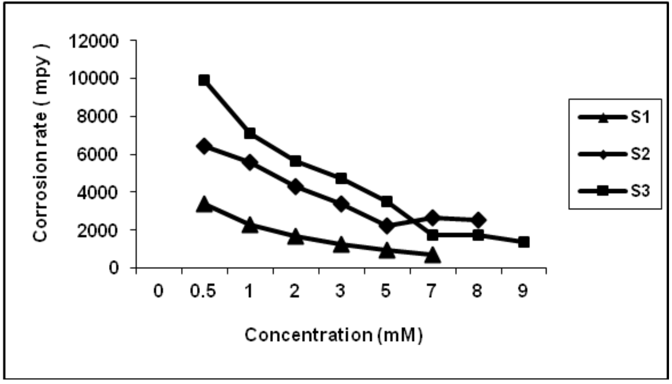


Fig. 4. Variation of Corrosion rate as function of concentration of inhibitors for the corrosion of mid steel in 1M H_2SO_4

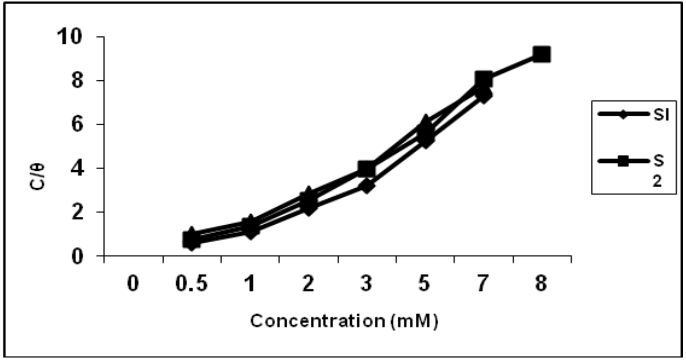


Fig 5. Langmuir's Plot of inhibitors in $1MH_2SO_4$

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 adsorption [19]. 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 temperature [20].

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.6

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

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

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

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 surface [21]. 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 energy [22]. This also indicates that these types of indicators are more effective at room temperature, compared to that of higher temperatures [23].

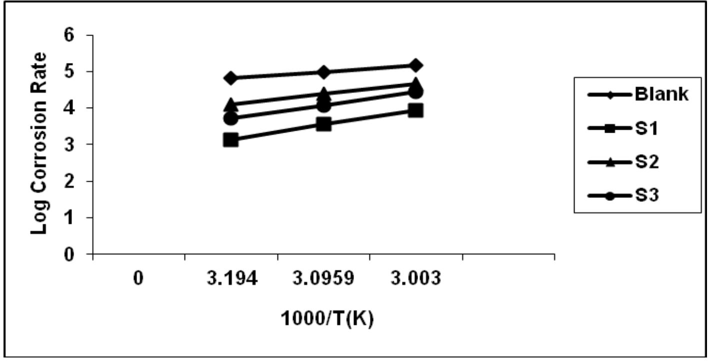


Fig 6. Arrhenius plot of corrosion rate of mild steel in 1M H2SO4 solution in the presence and absence of inhibitor

Electrochemical Studies - A.C Impedance measurements

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.7-9 and the data have been tabulated (Table 8).

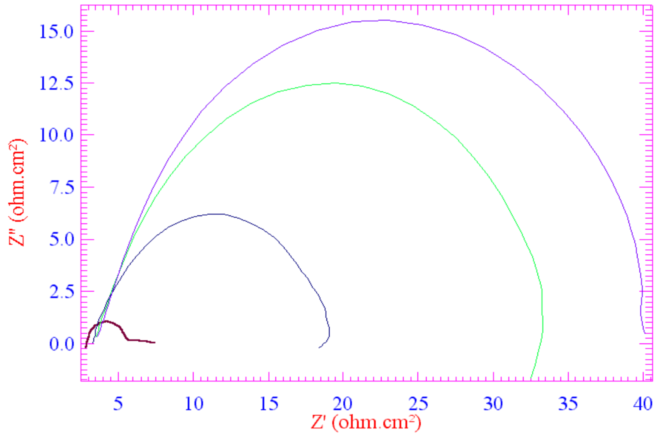
The charge transfer resistance (R_t) value for mild steel in uninhibited H_2SO_4 significantly changes after the addition of inhibitor. The value of charge transfer resistance increases with increase in concentration. The fact is advocated by the increase in inhibitor efficiency.

The semicircular nature of Nyquist plots obtained from all experiments indicate that corrosion of mild steel is controlled by charge transfer process as shown in Fig. (7-9).

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 [24, 25].

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. (10-12). 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).

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.



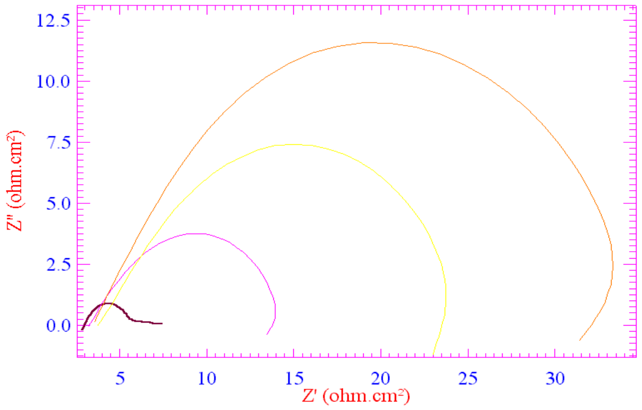


Fig 7. Nyquist diagrams for mild steel in 1M H_2SO_4 forselected concentration of S1

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 8. 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

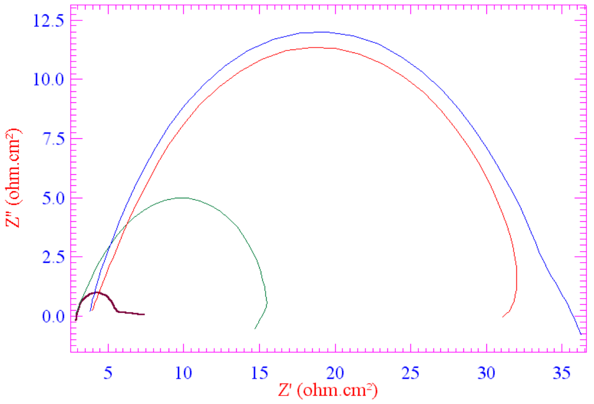


Fig 9 Nyquist diagrams for mild steel in 1M H_2SO_4 for selected concentration of S3

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

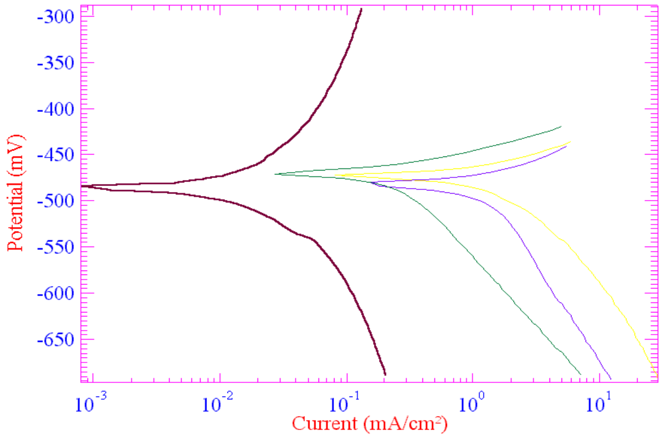


Fig 10. Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S1

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

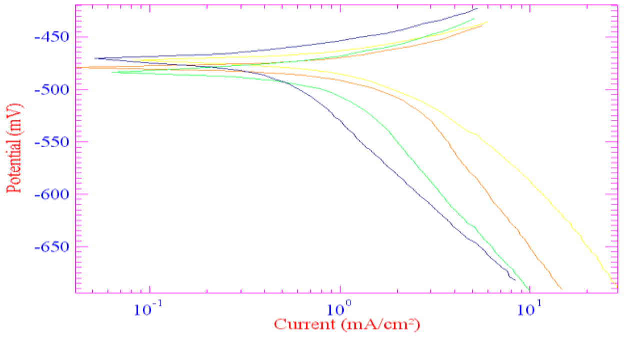


Fig 11. Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S2

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

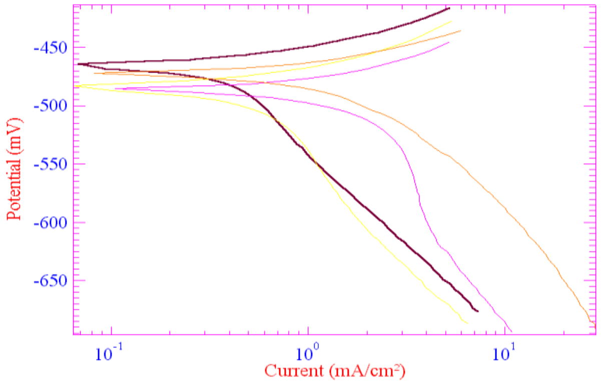


Fig 12. Polarization curves of mild steel recorded in 1M H_2SO_4 for selected concentration of inhibitor S3

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 [26, 27]

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.

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.13).Variations of inhibition effficiency, weight loss and corrosion rate with concentration were depicted in (Figs.14-16) in 1M HCl.

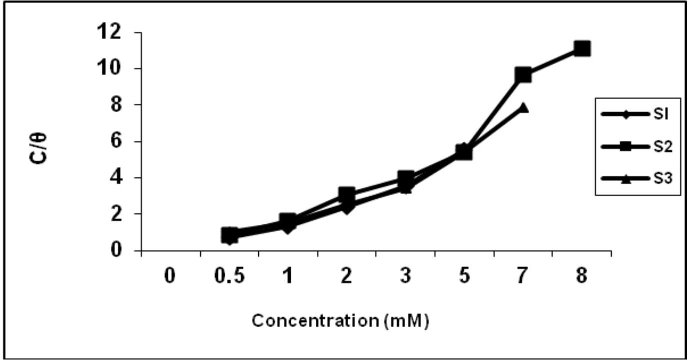


Fig 13. Langmuir's Plot of inhibitors in 1M HCI

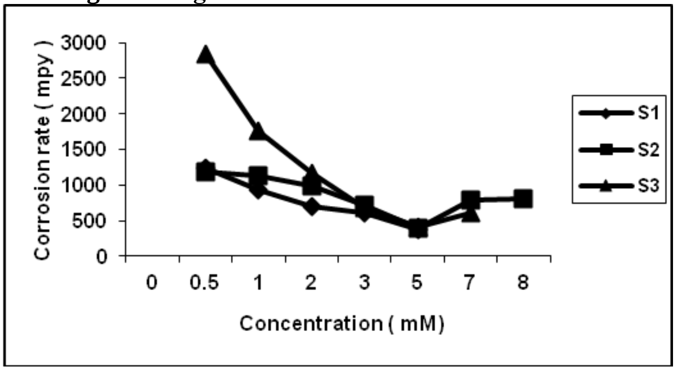


Fig 14. Variation of corrosion rate as an function of concentration of inhibitors for the corrosion of mild steel in 1M HCl

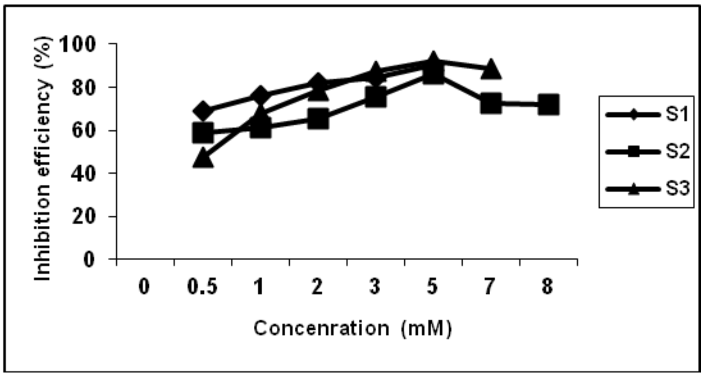


Fig 15. Variation of inhibitor efficiency with concentration of inhibitors at room temperature in 1M HCI

Nature of Inhibition

The inhibition efficiency of piperidin-4-one semicarbazones (S1, S2 and S3) may be due to adsorption of –NH and –CO groups of semicarbazone moiety.

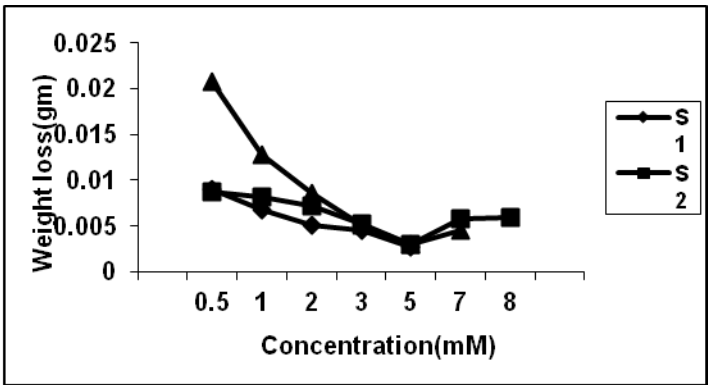


Fig 16. Plot of Weight loss (gms) Vs concentration (mM) for Inhibition of corrosion of mild steel in 1M HCI

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. 17. 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.18). This is due to the formation of adsorption layer of inhibitor on the metal surface.

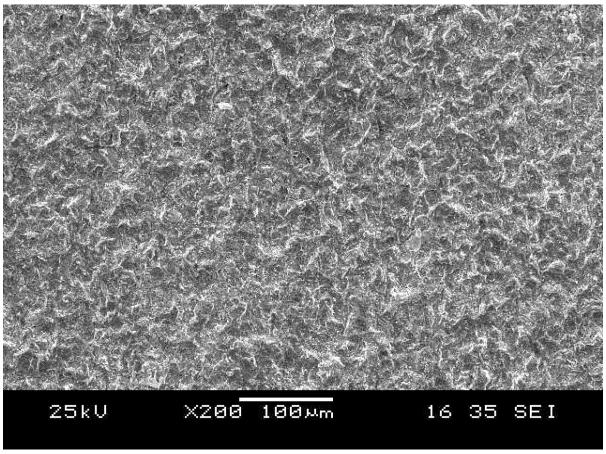


Fig 17. Scanning electron micrograph of mild steel sample after immersion in 1M H_2SO

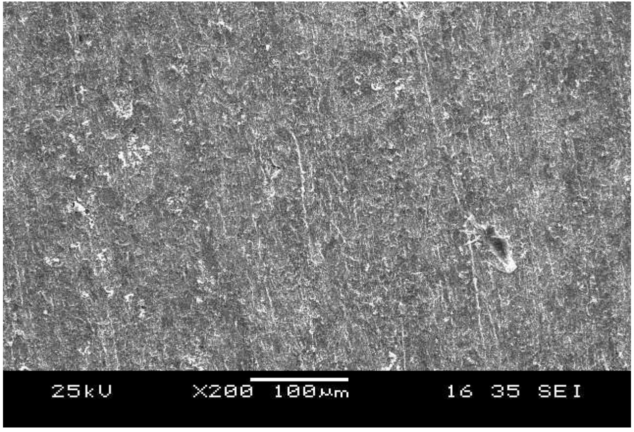


Fig 18. Scanning electron micrograph of mild steel sample after immersion in 1M H_2SO_4 in presence of ppm of inhibitors

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.

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)	$C_{18}H_{20}N_4O$	178-180°	65	70.20 (70.09)	6.29 (6.54)	18.01 (18.18)
(S^2)	$C_{20}H_{24}N_4O$	190-192°	70	71.22 (71.39)	7.03 (7.19)	16.52 (16.66)
(S^3)	$C_{21}H_{26}N_4O$	186-188°	65	71.39 (71.96)	7.62 (7.48)	16.04 (15.99)

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

Compound	ν (C=O)	ν (N^4-H)	ν ($N^4H)_{asym}$	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: ^{1}H NMR Chemical shift data (ppm) S1, S2 and S3

Compound	H-2	H-3		H-5		H-6	Aromatic Protons	Ring N-H	-CONH$_2$	-CONH	Other protons
		ax	eq	ax	eq						
S1	3.1 (dd)	1.93 (dd)	2.52 (bd)	2.36-2.42		3.75	7.2 -7.48 (m)	2.15(s)	5.7,6.2 (bd)	9.4(s)	
S2	3.64	2.45 (t)		2.18 (dd)	3.0 (dd)	3.9 (dd)	7.24 – 7.46 (m)	2.07(s)	5.3, 6.15 (b)	8.55(s)	1.25-1.54(m) 0.88(t)
S3	3.37 (d)	2.39 (d)		2.06 (dd)	3.04 (dd)	3.86 (dd)	7.28 – 7.44 (m)	2.03	5.4, 6.1(b)	9.27(s)	1.7(m),0.89,1.01

Table 4: ^{13}C 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, 128.6,128.7144.7,144.9

Table 5: Inhibition efficiencies, corrosion rate, Degree of coverage of various concentrations of inhibitors (S1, S2 & S3) for the corrosion of mild steel in1M 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

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

S1	Temperature ^{0}C	Inhibitor Concentration mM	Weight Loss (gms)	Inhibition Efficiency (%)	Corrosion Rate (mpy)
	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

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

Name of the inhibitors	E_a40^{o}C-60^{o}C KJ	ΔG^o_{ads} at various temperature (KJ)		
		40^{o}C	50^{o}C	60^{o}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

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

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 Concen. (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

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

Inhibitor	Inhibitor Concen. (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

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 Concen. (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

Conclusion

The three compounds were found to inhibit the corrosion of mild steel in 1M H_2SO_4 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.

1. Piperidin -4- one semicarbazones are effective inhibitors for corrosion of mild steel in 1M H_2SO_4 at optimum concentration of (5mM -8mM).
2. The inhibition efficiency increases with increasing inhibitor concentration.
3. All the compounds inhibit corrosion by adsorption mechanism and adsorption of these compounds from acid solution follow Langmuir's adsorption isotherm.
4. Higher values of thermodynamic activation function (Ea) for inhibited system than those for uninhibited acids show the temperature dependence on inhibition efficiency.
5. The negative ΔG^o values indicate the spontaneous adsorption of the inhibitors on the surface of mild steel.
6. Electrochemical impedance spectroscopy experiments have shown that an increase in inhibitor concentration causes an increase in polarization resistance R_t. where as a decrease in C_{dl} values, is due to the increase in thickness of the adsorbed layer.
7. The Tafel slopes obtained from potentiodynamic polarization curves indicate that all the compounds behave as mixed type inhibitors with more cathodic character in 1M H_2SO_4.
8. Addition of halide ions enhances inhibition efficiency.
9. It can be noted that S1, S2 and S3's inhibition performance is better in H_2SO_4 than in HCl.
10. Scanning Electron Microscope reveals the formation of a smooth, dense protective layer in the presence of inhibitor.

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