Inhibition of mild steel corrosion in sulfuric acid solution by thiadiazoles

M.A. QURAISHI* and S. KHAN

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, India
(*author for correspondence, e-mail: maquraishi@rediffmail.com)

Abstract

Four heterocyclic compounds namely 2-amino-1,3,4-thiadiazoles (AT), 5-Methyl-2-amino-1,3,4-thiadiazoles (MAT), 5-Ethyl-2-amino-1,3,4-thiadiazoles (EAT) and 5-Propyl-2-amino-1,3,4-thiadiazoles (PAT) were synthesized and their influence on the inhibition of corrosion of mild steel (MS) in 0.5 M H_2SO_4 was investigated by weight loss and potentiodynamic polarization techniques. The values of activation energy, free energy of adsorption, heat of adsorption, enthalpy of activation and entropy of activation were also calculated to investigate the mechanism of corrosion inhibition. Potentiodynamic polarization studies were carried out at room temperature, and showed that all the compounds studied are mixed type inhibitors causing blocking of active sites on the metal. The inhibition efficiency of the compounds was found to vary with concentration, temperature and immersion time. Good inhibition efficiency was evidenced in the sulfuric acid solution. The adsorption of the compounds on mild steel for sulfuric acid was found to obey Langmuir's adsorption isotherm. FT–IR spectroscopic studies were also used to investigate the purity of compounds synthesized.

1. Introduction

Heterocyclic compounds represent a potential class of corrosion inhibitors. There is a wide range of studies in the literature regarding corrosion inhibition by nitrogen-containing heterocyclic compounds [1–5]. Heterocyclic compounds containing both nitrogen and sulfur atoms are of particular importance as they often provides excellent inhibition compared with compounds containing only nitrogen or sulfur [6–10]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The planarity (π) and lone pair of electrons present on heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface.

The corrosion inhibiting behavior of thiadiazoles on mild steel have been reported in acidic media [11–14]. Heterocyclic thiadiazoles, besides being used as corrosion inhibitors, also find diverse application in biological and pharmacological activities [15–16].

In the present investigation, the corrosion inhibiting behavior of thiadiazoles, a new class of heterocyclic inhibitors, was investigated on mild steel in an acidic solution. The compounds were 2-amino-1,3,4-thiadiazoles (AT), 5-Methyl-2-amino-1,3,4-thiadiazoles (MAT), 5-Ethyl-2-amino-1,3,4-thiadiazoles (EAT) and 5-Propyl-2-amino-1,3,4-thiadiazoles (PAT).

2. Experimental details

Weight loss experiments were performed with cold rolled mild steel strips of size $2.0 \times 2.0 \times 0.25$ cm having composition, (wt %): 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P, and balance Fe as per standard method [17]. Double distilled water was used to prepare solutions of 0.5 M H_2SO_4. Thiadiazoles were synthesized as described by Kidwai et al. [15] and characterized through their spectral data; their purity was confirmed by thin layer chromatography. The names, molecular structures and molecular weights of the compounds are given in Table 1.

Potentiodynamic polarization studies were carried out using and EG&G (PAR model 173) potentiostat/galvanostat, a model 175 Universal programmer and a model 175 Universal programmer and a model RE 0089 $X–Y$ recorder. A platinum foil was used as counter electrode. All the experiments were carried out at a constant temperature of 28 ± 2 °C and at a scan rate of 1 mV s^{-1} at open current potential (o.c.p). The polarization curves were obtained after immersion of the electrode until a steady state was reached.

Table 1. Name, structures and molecular weights of the compounds used

S. No	Structure	Name and abbreviation	Relative Mol. weight
1.	[structure: N——N ring, H—S—, NH2]	2-amino-1, 3, 4- thiadiazole, AT	101
2.	[structure: N——N ring, H3C—S—, NH2]	5-methyl-2- amino-1, 3, 4- thiadiazole, MAT	115
3.	[structure: N——N ring, H5C2—S—, NH2]	5-ethyl-2-amino-1, 3, 4- thiadiazole, EAT	129
4.	[structure: N——N ring, H7C3—S—, NH2]	5-propyl-2-amino-1, 3, 4- thiadiazole, PAT	143

2.1. *FT–IR spectroscopy*

The FT–IR spectroscopic study was also used to investigate the purity of compound synthesized. The results are listed below:

1. 2-amino-1, 3, 4-thiadiazoles (AT) – IR (KBr): 3348 (NH_2), 1647 (C=N), 1311 (C–N), 600 (C–S) cm^{-1}.
2. 5-Methyl-2-amino-1, 3, 4-thiadiazoles (MAT) – IR (KBr): 3321 (NH_2), 1645 (C=N), 1316 (C–N), 650 (C–S), 1284 (CH_3–) cm^{-1}.
3. 5-Ethyl-2-amino-1, 3, 4-thiadiazoles (EAT) – IR (KBr): 3220 (NH_2), 1642 (C=N), 1316 (C–N), 653 (C–S), 1002 (CH_3CH_2–) cm^{-1}.
4. 5-Propyl-2-amino-1, 3, 4-thiadiazoles (PAT) – IR (KBr): 3044 (NH_2), 1653(C=N), 1285 (C–N), 657(C–S), 800 ($CH_3CH_2CH_2$–) cm^{-1}.

3. Results and discussion

3.1. *Weight loss*

Figure 1(a) shows the variation of inhibition efficiency with inhibitor concentration. The inhibition efficiency was obtained from weight loss measurements at different thiadiazoles concentrations at 30 °C. The percentage inhibition efficiency (e_{IE}) and surface coverage (θ) were calculated using the equations:

$$e_{IE} = \frac{(r_0 - r)}{r_0} \times 100 \tag{1}$$

$$\theta = \frac{(r_0 - r)}{r_0} \tag{2}$$

where r_0 and r are the corrosion rates in the absence and presence of inhibitor, respectively. The inhibition efficiency for all the compounds increases with increase in concentration. The maximum e_{IE} of each compound was achieved at 100 ppm and a further increase in
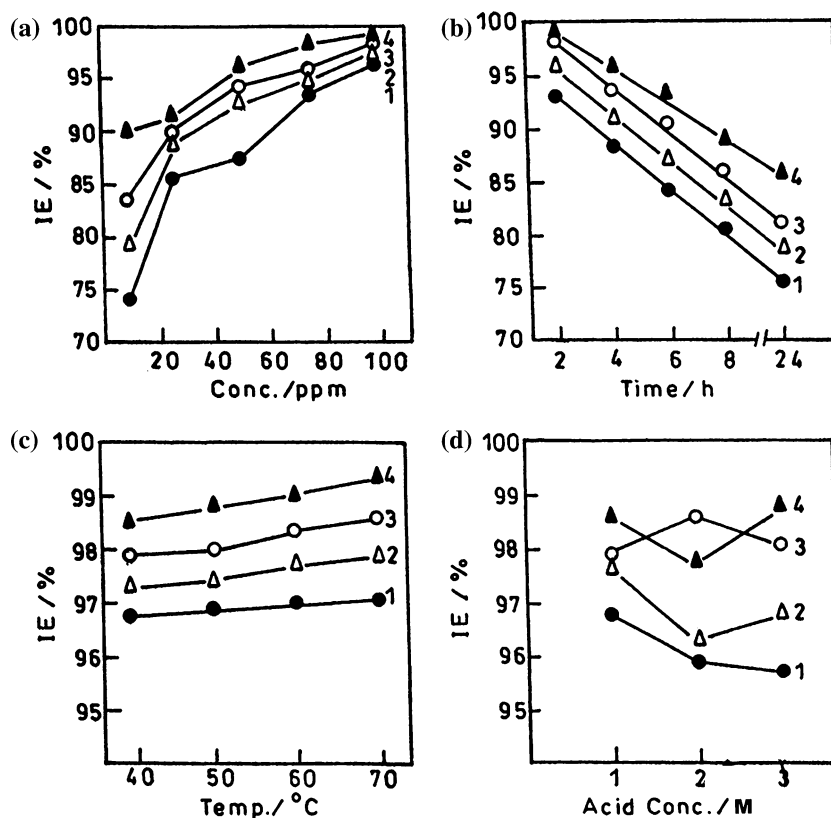

Fig. 1. Variation of inhibition efficiency with (a) inhibitor concentration, (b) immersion time, (c) solution temperature, (d) acid concentration in 0.5 M H_2SO_4 (1: AT; 2: MAT; 3: EAT; 4: PAT).
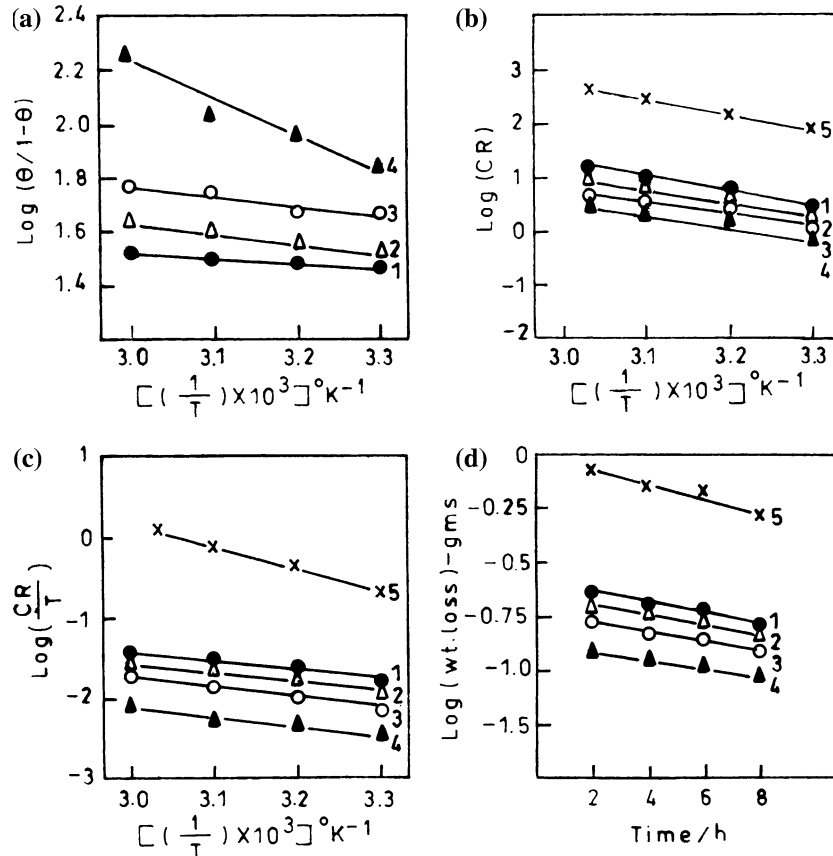
Fig. 2. Adsorption isotherm plot for (a) log ($\theta/1 - \theta$) vs. $1/T$, (b) log (CR) vs. I/T, (c) log (CR/T) vs. I/T in 1 N H_2SO_4, (d) half-life plot for log (weight loss) vs. immersion time in 0.5 M H_2SO_4 (1: AT; 2: MAT; 3: EAT; 4: PAT; 5: Blank).

concentration did not cause any appreciable change in performance.

The effect of immersion time on e_{IE} is shown in Figure 1(b). e_{IE} for all compounds decreases with increase in immersion time from 2 to 24 h. The decrease in inhibition efficiency with time may be attributed to various factors such as an increase in the cathodic or reaction rate or increase in the ferrous ion concentration [18]. The influence of temperature on e_{IE} is shown in Figure 1 (c). e_{IE} increases with increase in temperature from 30 to 60 °C indicating that the inhibitor molecules are stable at higher temperatures. The variation of e_{IE} with increase in acid concentration is shown in Figure 1(d); it is clear that e_{IE} shows no significant change with increase in acid concentration from 0.5 to 1.5 M H_2SO_4.

The degree of surface coverage (θ) for different inhibitor concentrations in 0.5 M H_2SO_4 at 30 °C over

2 h immersion time was evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. A plot of log ($\theta/1$-θ) vs. $1/T$ is shown in Figure 2(a). The plot gives the values for calculating the heat of adsorption (Q) with a slope ($-Q/2.303R$). The values for the heat of adsorption are shown in Table 2. The values of heat of adsorption for all the inhibitors are less than (-40 kJ mol^{-1}); this indicates physical adsorption [19].

It has been reported by a number of authors [20–22] that, in acid solution, the logarithm of the corrosion rate is a linear function of $1/T$ (Arrhenius equation):

$$\text{Log (Rate)} = \frac{-E_a^0}{2.303RT} + A \qquad (3)$$

where, E_a^0 is the apparent effective activation energy, R the general gas constant and A the Arrhenius pre-exponential factor. A plot of log of corrosion rate

Table 2. Thermodynamic activation parameters for mild steel in 0.5 M H_2SO_4 in absence and presence of inhibitors of 100 ppm concentration

System	E_a/kJ mol^{-1}	ΔH/kJ mol^{-1}	$-\Delta S$/J mol^{-1}K^{-1}	$-\Delta G_{ads}$/kJ mol^{-1}	$-Q$/kJ mol^{-1}
0.5 M H_2SO_4	57.33	57.40	197.59	–	–
AT	52.84	103.00	226.31	38.01	5.74
MAT	51.44	60.90	228.23	38.87	11.43
EAT	46.95	73.60	230.15	39.99	19.14
PAT	38.23	47.85	235.89	42.23	38.2

obtained by weight loss measurement vs. $1/T$ gave straight lines as shown in Figure (2b). The values of activation energy (E_a^0) obtained from the slope of the lines are given in Table 2. An alternative formula for the Arrhenius equation is the transition state equation:

$$\text{Rate} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^0}{R}\right)\exp\left(-\frac{\Delta H^0}{RT}\right) \quad (4)$$

where, h is the Plank constant, N the Avogadro number, ΔS^0 the entropy of activation, and ΔH^0 the enthalpy of activation. A plot of log (CR/T) vs. $1/T$ should give a straight line, Figure (2c), with a slope of ($-\Delta H^0/2.303\ R$) and an intercept of [(log (R/Nh) + ($\Delta S^0/2.303\ R$)], from which the values of ΔS^0 and ΔH^0 were calculated; those are listed in Table 2. The data show that thermodynamic activation functions (E_a^0) of the corrosion in mild steel in 0.5 M H_2SO_4 solution in the presence of the inhibitors are lower than those in the free acid solution, indicating that all the inhibitors exhibit high e_{IE} at elevated temperatures [23]. Such inhibitors are bound to the surface by specific adsorption forces or by chemisorption as a result of which a surface film of reaction product is formed [19]. The chemisorption process in the film formation with a strong attractive force is likely to be exothermic resulting in lowering of the activation energy [24]. The result of ΔH^0 (Table 2) is in the order AT > EAT > MAT > PAT which is indicative of the order of energy barrier at elevated temperature [23]. The values of activation ΔS^0 in the absence and presence of the inhibitors are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [25]. The average value for free energy of adsorption (ΔG_{ads}), calculated using the following equations [26] are given in Table 2.

$$\Delta G_{ads} = -RT\ln(55.5\,K) \quad (5)$$

and K is given by:

$$K = \theta/C(1-\theta) \quad (6)$$

where, θ is degree of coverage on the metal surface, C is concentration of inhibitor in mol l^{-1}, K is equilibrium constant, R is the gas constant and T is temperature. It is found that the ΔG_{ads} values for all the compound at higher temperature is more than -40 kJ mol^{-1} indicating
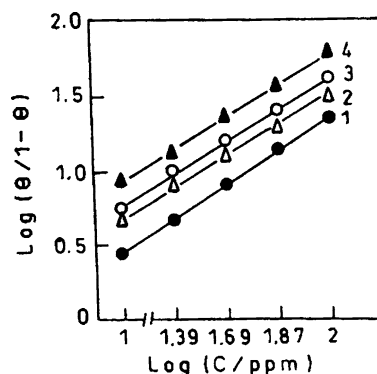

Fig. 3. Langmuir's adsorption isotherm plot for the adsorption of various inhibitors in 0.5 M H_2SO_4 (1: AT; 2: MAT; 3: EAT; 4: PAT).

that the thiadiazoles are chemically adsorbed on the metal surface [27].

The low and negative value of ΔG_{ads} indicate spontaneous adsorption of inhibitor on the surface of mild steel [28]. It was also found that value of activation energy of the inhibited systems were lower than that of the uninhibited system. Putilova [23] has indicated that this type of inhibitor is effective at higher temperatures.

The plot of log (weight loss) vs. immersion time Figure (2d), gave a straight line indicating that the reaction is first order reaction. The value of the rate constant was calculated using the first order rate law [29].

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} \quad (7)$$

where $[A_0]$ is the initial mass of the metal and $[A]$ is the mass corresponding to time t. The half-life ($t_{1/2}$) values were calculated using equation [30].

$$t_{1/2} = 0.693/k \quad (8)$$

and weight loss is expressed in grams.

The values of rate constants and half-life ($t_{1/2}$) obtained from the above relations are summarized in Table 3. Half-life values were found to be constant at different immersion times. The order of effectiveness of inhibitors were observed as PAT > EAT > MAT > AT in 0.5 M H_2SO_4. The constant values of rate constant further confirmed that the corrosion of mild steel in 0.5 M H_2SO_4 in presence of different inhibitors follows first order kinetics.

Table 3. First order rate constant and Half-life values in hours (h) for the corrosion of mild steel in 0.5 M H_2SO_4 in absence and presence of inhibitors of 100 ppm concentration at 30 °C

System	10^{-3} k	$t_{1/2}$
0.5 M H_2SO_4	4.960 ± 0.126	138.71
AT	6.726 ± 0.321	103.03
MAT	5.400 ± 0.294	128.33
EAT	3.527 ± 0.241	196.48
PAT	3.073 ± 0.133	225.51

Table 4. Electrochemical polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 containing 100 ppm inhibitors at 30 °C

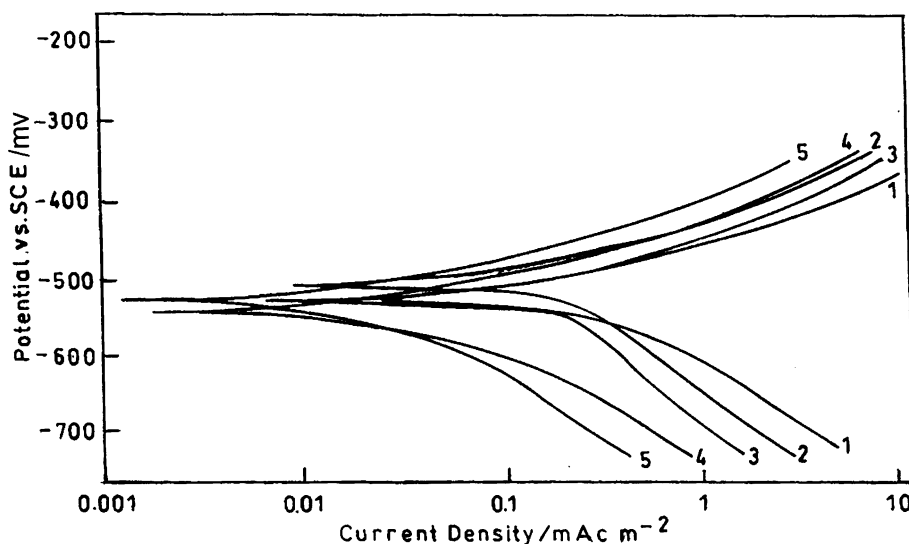| System	0.5 M H_2SO_4		
	E_{corr}/mV	I_{corr}/mA	e_{IE}/%
0.5 M H_2SO_4	−533.00	0.360	–
AT	−513.00	0.100	72.22
MAT	−537.00	0.095	73.61
EAT	−547.00	0.040	88.89
PAT	−530.00	0.029	91.94

Fig. 4. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 (1: Blank; 2: AT; 3: MAT; 4: EAT; 5: PAT).

3.2. *Adsorption isotherm*

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [31]. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight-loss data. Data were tested graphically by fitting to various isotherms. A plot of log $\theta/(1-\theta)$ vs. log C shows a straight line (Figure 3) indicating that adsorption follows the Langmuir isotherm.

$$\theta/(1 - \theta) = kC\exp(-G_{ads}/RT) \qquad (9)$$

where G_{ads} is the free energy of adsorption and C is the inhibitor concentration.

3.3. *Potentiodynamic polarization*

The cathodic and anodic polarization curves of mild steel in 0.5 M H_2SO_4 in the absence and presence of different inhibitors at 100 ppm concentration at 28 ± 2 °C are shown in Figure 4. Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and e_{IE} were calculated from Tafel plots and are given in Table 4. A maximum decrease in I_{corr} was observed for PAT. E_{corr} values show that all these compounds are mixed type inhibitors in sulfuric acid.

3.4. *Mechanism of corrosion inhibition*

Inhibition of mild steel corrosion in acidic solutions by thiadiazoles can be explained on the basis of adsorption. These compounds inhibit corrosion by controlling both the anodic and cathodic reactions. In acidic solutions the compounds exist as protonated species. These protonated species adsorb on the cathodic sites through the π-electrons of the aromatic ring and the lone pair of electrons of nitrogen and sulfur atoms [31].

Among the compounds investigated, the order of e_{IE} is:

$$PAT > \quad EAT > \quad MAT > \quad AT$$
$$(C_3) \qquad (C_2) \qquad (C_1) \qquad (H)$$

The presence of the propyl group in PAT increases the density of electrons on the sulfur and nitrogen atoms caused by resonance effects, which facilitate stronger adsorption of PAT on the mild steel surface. This leads to higher e_{IE} of PAT than EAT compared with MAT and AT. The e_{IE} decreases with decrease in the number of carbon atoms as a consequence of the decrease in the electron density on the nitrogen and sulfur atoms.

4. Conclusions

(i)   All the thiadiazoles acted as efficient corrosion inhibitors up to 1.5 M H_2SO_4,
(ii) All the compounds inhibited corrosion of mild steel by adsorption,
(iii) Adsorption of thiadiazoles on the mild steel surface in H_2SO_4 solution obeyed Langmuir's adsorption isotherm, and
(iv) All the compounds examined acted as mixed type inhibitors in 0.5 M H_2SO_4.

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