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Hector bases – a new class of heterocyclic corrosion inhibitors for mild steel in acid solutions

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Abstract

Three heterocyclic compounds namely 3-anilino-5-imino-4-phenyl-1, 2,4-thiadiazoline (AIPT), 3-anilino-5-imino-4-tolyl-1, 2,4-thiadiazoline (AITT), and 3-anilino-5-imino-4-chlorophenyl-1, 2,4-thiadiazoline (AICT) were synthesized and their influence on the inhibition of corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 was investigated by weight loss and potentiodynamic polarization techniques. The values of activation energy and free energy of adsorption of these compounds were also calculated. Potentiodynamic polarization studies were carried out at room temperature, and showed that all the compounds were 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 both acid solutions. The adsorption of the compounds on mild steel for both acids was found to obey the Langmuir adsorption isotherm. Electrochemical impedance spectroscopy was also used to investigate the mechanism of corrosion inhibition.

1. Introduction

Heterocyclic compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by nitrogen–containing heterocyclic compounds [1–8]. Heterocyclic compounds containing both nitrogen and sulfur atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur [9–14]. The corrosion-inhibiting property of these compounds is attributable to their molecular structure. The planarity (π) and the number of lone pairs of electrons present on heteroatoms are the important structural features that determine adsorption on the metal surface.

In the present investigation, the corrosion inhibiting behavior of thiadiazoline, a new class of heterocyclic compounds, was investigated on mild steel in acidic solutions. The compounds were 3-anilino-5-imino-4-phenyl-1, 2,4-thiadiazoline (AIPT), 3-anilino-5-imino-4-tolyl-1, 2,4-thiadiazoline (AITT) and 3-anilino-5-imino-4-chlorophenyl-1, 2,4-thiadiazoline (AICT).

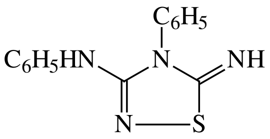
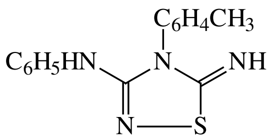
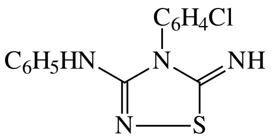
2. Experimental details

Weight loss experiments were performed with cold rolled mild steel strips of size 2.0 cm × 2.0 cm × 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 methods [15]. The acids HCl and H_2SO_4 (Merck) of AR grade were used for preparing solutions. Double distilled water was used to prepare solutions of 1 M HCl and 0.5 M H_2SO_4. Thiadiazolines were synthesized as described by Butler et al. [16] 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 an EG&G (PAR model 173) potentiostat/galvanostat, a model 175 Universal programmer and a model RE 0089 X–Y recorder. A platinum foil was used as the auxiliary electrode, a saturated calomel electrode was used as reference and mild steel was used as working 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.

Impedance measurements were performed for mild steel in 1 M HCl in the absence and presence of 500 ppm of AICT at E_{corr} with the a.c. voltage amplitude ± 5 mV in the frequency range 5 Hz–100 kHz. A time interval of a few minutes was given for the o.c.p. to reach a steady value. All the measurements were carried out with an

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

S.No	Structure	Name and abbreviation	Mol. weight
1.		3-anilino-5-imino-4-phenyl-1,2,4-thiadiazoline (AIPT)	268
2.		3-anilino-5-imino-4-tolyl-1,2,4-thiadiazoline (AITT)	282
3.		3-anilino-5-imino-4-chlorophenyl-1,2,4-thiadiazoline (AICT)	302

EG&GPAR (model 273A) potentiostat/galvanostat, and an EG&G (PAR model 5301A) lock-in-amplifier, using an IBM computer at 28 ± 2 °C.

3. Results and discussion

3.1. *Weight loss*

Figures 1(a) and 2(a) show the variation of inhibition efficiency with inhibitor concentration. The inhibition efficiency was obtained from weight loss measurements at different concentrations of thiadiazolines at 25 °C. The percentage inhibition efficiency (e_{IE}) and surface coverage (θ) of each concentrations were calculated using the following equations:

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

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

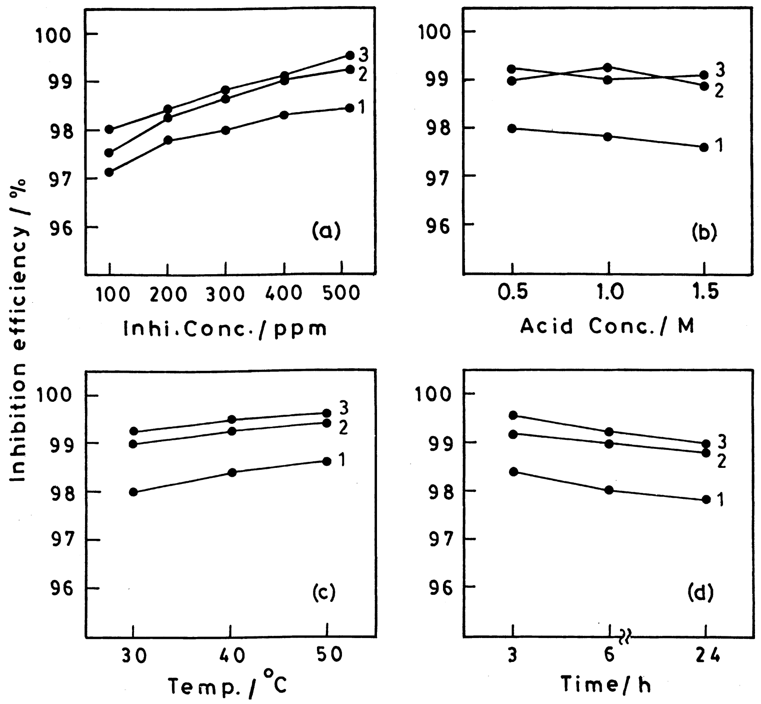


Fig. 1. Variation of inhibition efficiency with (a) inhibitor concentration, (b) acid concentration, (c) solution temperature, (d) immersion time in 0.5 M H_2SO_4. (1: AIPT; 2: AITT; 3: AICT).

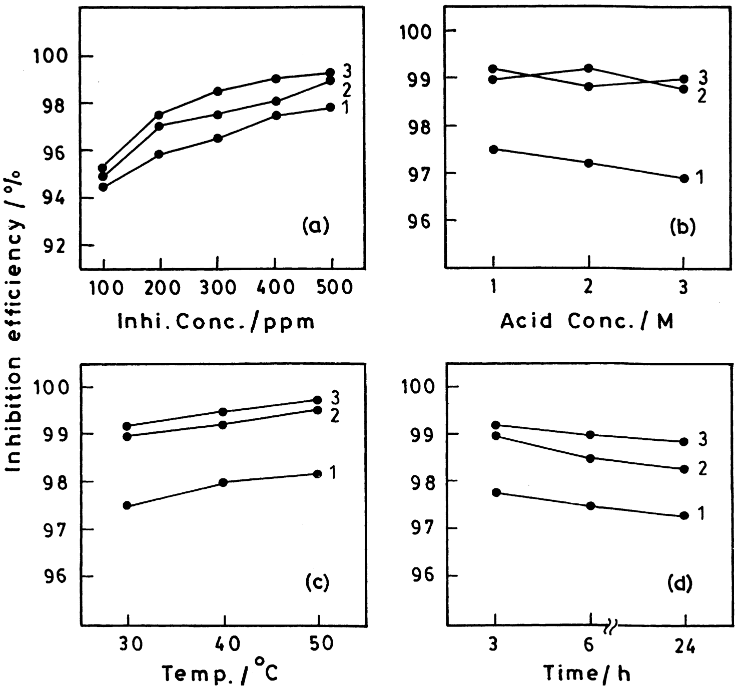


Fig. 2. Variation of inhibition efficiency with (a) inhibitor concentration, (b) acid concentration, (c) solution temperature, (d) immersion time in 1 M HCl. (1: AIPT; 2: AITT; 3: AICT).

where r_0 and r are the corrosion rates in the absence and presence of inhibitors, respectively . It has been observed that the inhibition efficiency for all these compounds increases with increase in concentration. The maximum e_{IE} of each compound was achieved at 500 ppm and a further increase in concentration did not cause any appreciable change in the performance of the inhibitor.

The variation of e_{IE} with increase in acid concentration is shown in Figure 1(b) and 2(b), it is clear that e_{IE} of all these compounds shows no significant change with increase in acid concentration from 1 to 3 M HCl and 0.5–1.5 M H_2SO_4. The influence of temperature on e_{IE} is shown in Figure 1(c) and 2(c). e_{IE} of all the compounds increases with increase in temperature from 30 to 50 °C indicating that inhibitor molecules are stable at higher temperatures,. The effect of immersion time on e_{IE} is shown in Figures 1(d) and 2(d). It is found that e_{IE} for all the compounds decreases with increase in immersion time.

The values of activation energy (E_a) were calculated using the Arrhenius equation [17, 18].

$$\ln(r_2/r_1) = -E_a\Delta T/(R \times T_2 \times T_1) \quad (3)$$

where r_1 and r_2 are corrosion rates at temperature T_1 and T_2, respectively, and $\Delta T = (T_2 - T_1)$.

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the equation.

$$\Delta G_{ads} = -RT\ln(55.5K) \quad (4)$$

where $K = \theta/C\,(1-\theta)$, θ is the degree of coverage on the metal surface, C is the concentration of inhibitor in mol l^{-1} , ΔG_{ads} is the free energy of adsorption in kJ mol^{-1} and K is the equilibrium constant. The values of E_a and ΔG_{ads} are given in Table 2. E_a values for inhibited systems are lower than those for uninhibited system indicating that all the inhibitors exhibit high e_{IE} at elevated temperatures [19]. The negative values of ΔG_{ads} suggest the strong interaction of the inhibitor molecules whereas low values of ΔG_{ads} indicated spontaneous adsorption of inhibitors on the mild steel surface [20, 21].

Table 2. Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 0.5 M H_2SO_4 and 1 M HCl in the absence and presence of 500 ppm concentration of various inhibitors

System	E_a /kJ mol^{-1}	$-\Delta G_{ads}$ /kJ mol^{-1} 30 °C	40 °C	50 °C
0.5 M H_2SO_4	29.42	–	–	–
AIPT	15.38	35.69	37.49	39.04
AITT	13.04	37.91	40.04	41.92
AICT	22.48	38.41	40.88	42.55
1 M HCl	53.58	–	–	–
AIPT	40.04	35.11	36.86	38.37
AITT	28.71	37.78	39.62	42.13
AICT	22.86	38.12	40.67	42.67

3.2. *Adsorption isotherm*

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbates on the metal surface must be known [22]. The surface coverage values (θ) were evaluated using corrosion rate

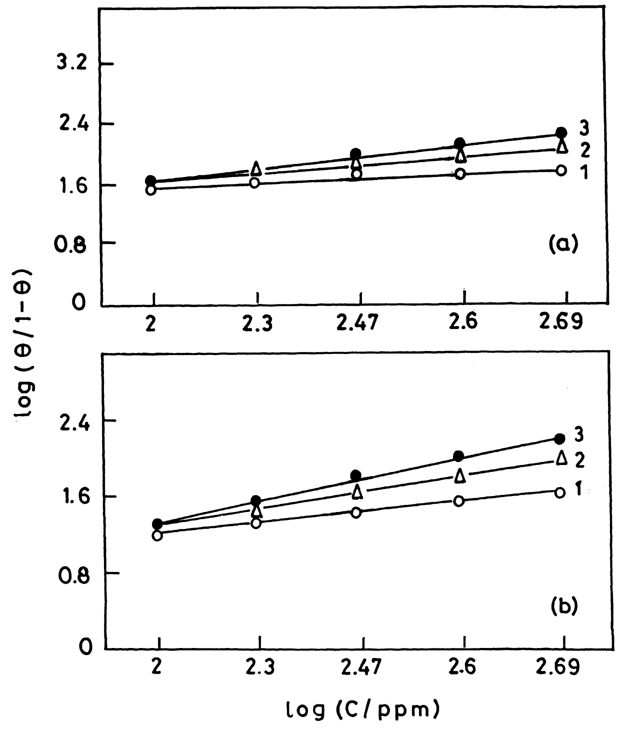


Fig. 3. Langmuir adsorption isotherm plots for the adsorption of various inhibitors in (a) 0.5 M H_2SO_4 and (b) 1 M HCl (1: AIPT; 2: AITT; 3: AICT).

values (r) obtained from the weight loss method. The θ values for different inhibitor concentrations were tested by fitting to various isotherms. A plot of $\log\theta/(1-\theta)$ against log C shows a straight line indicating that adsorption from both acids follows the Langmuir adsorption isotherm (Figure 3(a) and (b)) [23].

3.3. *Potentiodynamic polarization*

The cathodic and anodic polarization curves of mild steel in 1 M HCl and 0.5 M H_2SO_4 in the absence and presence of different inhibitors at 500 ppm concentration at 28 ± 2 °C are shown in Figure 4(a) and (b). 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 3. A maximum decrease in I_{corr} was observed for AICT. E_{corr} values show that all these compounds are mixed type inhibitors in both acids.

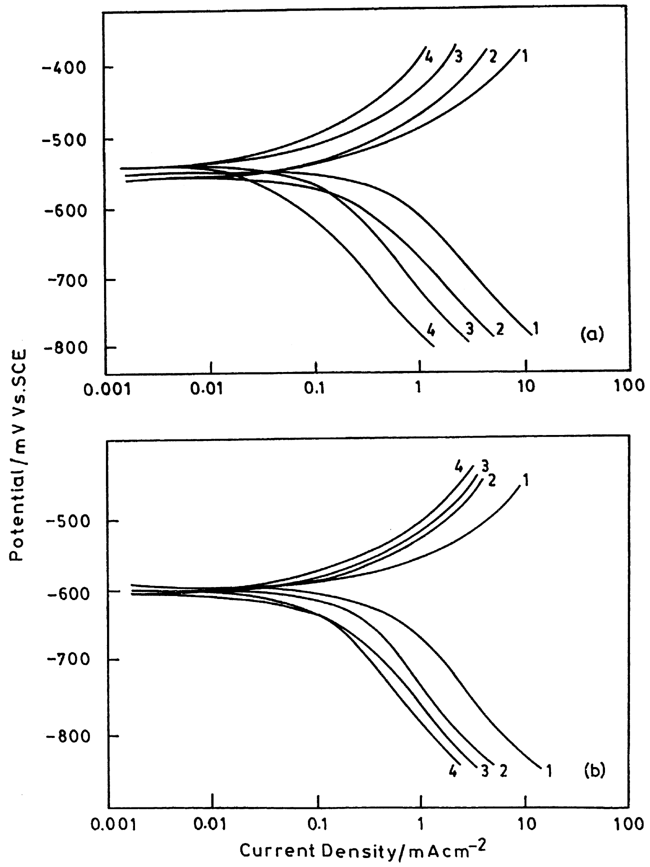


Fig. 4. Potentiodynamic curves for mild steel in (a) 0.5 M H_2SO_4 and (b) 1 M HCl in the presence and absence of 500 ppm of various inhibitors (1: Blank; 2: AIPT; 3: AITT; 4: AICT).

3.4. *Electrochemical impedance*

Impedance diagrams obtained for the frequency range 5 Hz–100 kHz at E_{corr} for mild steel in 1 M HCl are shown in Figure 5(a) and (b). The Nyquist plots are not perfect semicircles, which may be attributed to frequency dispersion [24]. The values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were obtained using Nyquist and Bode plots, respectively (Figure 5). R_t values were calculated from the difference in impedance at lower and higher frequencies as reported elsewhere [25]. C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum ($Z_{im,max}$) using the following relation:

Table 3. Electrochemical polarization parameters for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl in the absence and presence of 500 ppm concentration of various inhibitors

System	0.5 M H_2SO_4			1 N HCl		
	E_{corr} /mV	I_{corr} /mA cm^{-2}	e_{IE} /%	E_{corr} /mV	I_{corr} /mA cm^{-2}	e_{IE} /%
Blank	−550	0.36	–	−596	0.35	–
AIPT	−560	0.11	69.4	−600	0.11	68.5
AITT	−540	0.072	80.0	−610	0.088	74.8
AICT	−540	0.035	90.3	−600	0.071	79.7

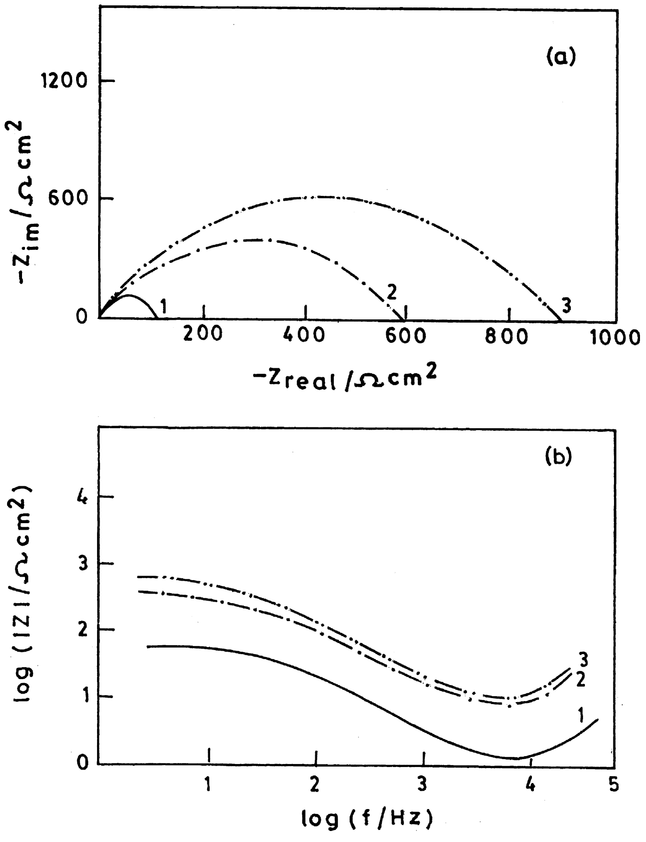


Fig. 5. Impedance analysis for mild steel in 1 M HCl in the presence and absence of 500 ppm of various inhibitors (a) Nyquist plot and (b) Bode plot (1: 0 ppm; 2: 100 ppm; 3: 500 ppm).

Table 4. Electrochemical impedance parameters for the corrosion of mild steel in 1 M HCl containing different concentrations of AICT at room temperature

Concentration /ppm	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	e_{IE} /%
1 M HCl	100	1585.03	–
AICT			
100	600	501.87	83.4
500	900	316.22	88.9

$$C_{dl} = \frac{1}{2\pi f_{max}} \frac{1}{R_t} \tag{5}$$

The percentage e_{IE} was calculated using Equation 6:

$$e_{IE} = \frac{(1/R_{t0}) - (1/R_{ti})}{(1/R_{t0})} \times 100 \tag{6}$$

where R_{t0} and R_{ti} are the charge transfer resistances without and with inhibitor, respectively, and are given in Table 4. Values of R_t increase with increase in inhibitor concentration (AICT) and this in turn leads to an increase in inhibition efficiency. The addition of AICT to 1 M HCl lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption [26].

3.5. *Mechanism of corrosion inhibition*

Inhibition of mild steel corrosion in acidic solutions by thiadiazolines can be explained on the basis of adsorption. These compounds inhibit the 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 of the mild steel and decrease the evolution of hydrogen. Adsorption on anodic sites occurs through the π-electrons of aromatic rings and the lone pair of electrons of nitrogen and sulphur, atoms, which decreases anodic dissolution of mild steel [27]. The highest e_{IE} obtained for the chloroderivative (AICT) is due to the fact that its dipole moment is greater than that of the parent compound (AIPT). Smialowska et al. observed similar behaviour for chlorosubstituted thiophene derivatives [28]. Gad - Allah et al. and Quraishi et al. have reported that chloro heterocyclic compounds give higher inhibition efficiency than the parent compound [29, 30].

4. Conclusions

The investigated compounds show excellent performance as corrosion inhibitors in both hydrochloric and sulfuric acid media. They inhibit the corrosion of mild steel in acid solutions by an adsorption mechanism and the adsorption follows the Langmuir adsorption isotherm.

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