Inhibition of mild steel corrosion in the presence of fatty acid triazoles

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Abstract

The influence of some fatty acid triazoles namely, 4-Phenyl-5-undecyl-4H- [1,2,4] triazole-3-thiol (PUTT), 5-Heptadec-8-enyl-4-phenyl-4H- [1,2,4] triazole-3-thiol (HPTT), and 5-Dec-9-enyl-4-phenyl-4H- [1,2,4] triazole-3-thiol (DPTT) on the corrosion of mild steel in 1 M hydrochloric acid (HCl) and 0.5 M sulfuric acid (H_2SO_4) was studied by weight loss and potentiodynamic polarization methods. The values of activation energy and free energy of adsorption of all the triazoles were calculated to investigate the mechanism of corrosion inhibition. The potentiodynamic polarization studies were carried out at room temperature, according to which all the compounds were mixed type inhibitors and inhibit the corrosion of mild steel by blocking the active sites of the metal. The adsorption of all the triazoles on mild steel surface in both the acid solutions was found to obey the Langmuir adsorption isotherm. All the compounds showed good inhibition efficiency in both acids. The inhibition efficiency of the compounds was found to vary with their nature and concentration, solution temperature and immersion time. Electrochemical impedance spectroscopy was also used to investigate the mechanism of the corrosion inhibition.

1. Introduction

Organic compounds containing both nitrogen and sulfur atoms are of particular interest as they give better inhibition efficiency than those containing N or S alone [1–3]. Among these thiourea and its derivatives have been investigated extensively [4–8]. Schmitt [9] has reported that thiourea derivatives are toxic and induce permeation of hydrogen into the metal causing hydrogen embrittlement; therefore, the use of these compounds is not safe.

In previous work we have studied the effects of a few triazoles having small alkyl group in a triazole ring on the corrosion inhibition of mild steel in acidic solutions [10, 11]. In the present investigation we report the influence of three triazole based compounds having long chain carbon atoms in a triazole ring: namely, 4-phenyl-5-undecyl-4H- [1,2,4] triazole-3-thiol (PUTT), 5-Heptadec-8-enyl-4-phenyl-4H- [1,2,4] triazole-3-thiol (HPTT), and 5-Dec-9-enyl-4-phenyl-4H- [1,2,4] triazole-3-thiol (DPTT) on corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4.

The choice of the inhibitors is based on the following considerations: (i) they possess a lone pair of electrons on sulfur and nitrogen atoms additional to the π electrons of 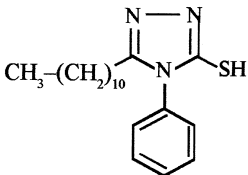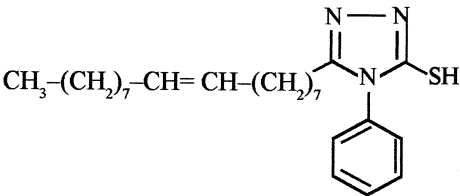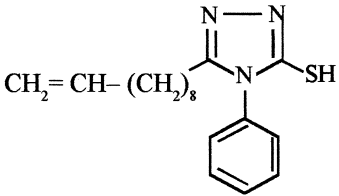the phenyl and triazole ring through which they can adsorb readily on the metal surface, and (ii) their toxicity is low.

2. Experimental details

Weight loss experiments were performed with cold rolled mild steel strips of size 2 cm × 2.5 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 method [12]. 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. The triazoles of fatty acid were synthesized as described by Kitture et al. [13] and characterized by their infrared spectra and the purity of the compounds was checked by thin layer chromatography. The names and molecular structures 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 the reference electrode and mild steel was used as working electrode. All the experiments were carried out

Table 1. Name and structure of fatty acid triazoles used

S.No.	Structure	Designation and abbreviation
1	$CH_3-(CH_2)_{10}$ — triazole-thiol with SH and N—N, phenyl	4-Phenyl-5-undecyl-4H- [1,2,4] -triazole-3-thiol (PUTT)
2	$CH_3-(CH_2)_7-CH= CH-(CH_2)_7$ — triazole-thiol with SH and N—N, phenyl	5-Heptadec-8-enyl-4-phenyl-4H- [1,2,4] -triazole-3-thiol (HPTT)
3	$CH_2= CH- (CH_2)_8$ — triazole-thiol with SH and N—N, phenyl	5-Dec-9-enyl-4-phenyl-4H- [1,2,4] -triazole-3-thiol (DPTT)

at constant temperature of 28 ± 2 °C and at a scan rate of 1 mV s^{-1} at o.c.p. The polarization curves were obtained after immersion of the electrode in the solution 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 DPTT 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 open circuit potential (o.c.p.) to read a steady value. All the measurements were carried out with an EG&GPAR (model 273A) potentiostat/galvanostat, and an EG&G (PAR model 5301A) lock-in-amplifier, using an IBM computer at 28 ± 2 °C.

Analysis of the samples was accomplished using an Auger electron spectroscope (Varian CMA VT–112). Polished specimens were dipped in inhibited acid solution containing 500 ppm DPTT as described previously [14]. The beam energy of 3 keV was used to obtain the Auger spectra. The resolution depth was in the range 0.2–2 nm.

3. Results and discussion

3.1. *Weight loss*

Figures 1(a) and (d) show the variation of inhibition efficiency with inhibitor concentration. The inhibition efficiency was obtained from weight loss measurements at different concentrations of triazoles at 35 °C. The percentage inhibition efficiency (e_{IE}) and surface coverage (θ) of each concentrations were calculated using the following equations:

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

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

where r_o 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 concentrations. The maximum e_{IE} of each compound was achieved at 500 ppm. In general, for pickling of steel, as pointed out by Machu [15] and Turgoose et al. [16], sulfur containing compounds are preferred for H$_2$SO$_4$ solution and nitrogen containing compounds for HCl solution. Every et al. [17] and Schmitt [9] reported that a mixture of nitrogen and sulfur compounds are often better than either type alone. The compounds studied contain both nitrogen and sulfur atoms hence they have exhibited good performance ($e_{IE} > 87\%$) on the corrosion of MS in 1 M HCl and 0.5 M H$_2$SO$_4$ even at a concentration as low as 25 ppm.

The influence of temperature at maximum concentration (i.e., 500 ppm) on e_{IE} is shown in Figure 1(b) and (e). The inhibition efficiency for all the triazoles except PUTT in 1 M HCl decreases slightly with increase in temperature from 35 to 65 °C, while in case of PUTT the inhibition efficiency does not change with rise in temperature from 35 to 65 °C showing that the inhibitors are effective at higher temperature up to 65 °C.

The variation of inhibition efficiency of all the three fatty acid triazoles with immersion time is shown in Figure 1(c) and (f). No significant change in inhibition efficiency occurs with increase in immersion time from 2 to 6 h.
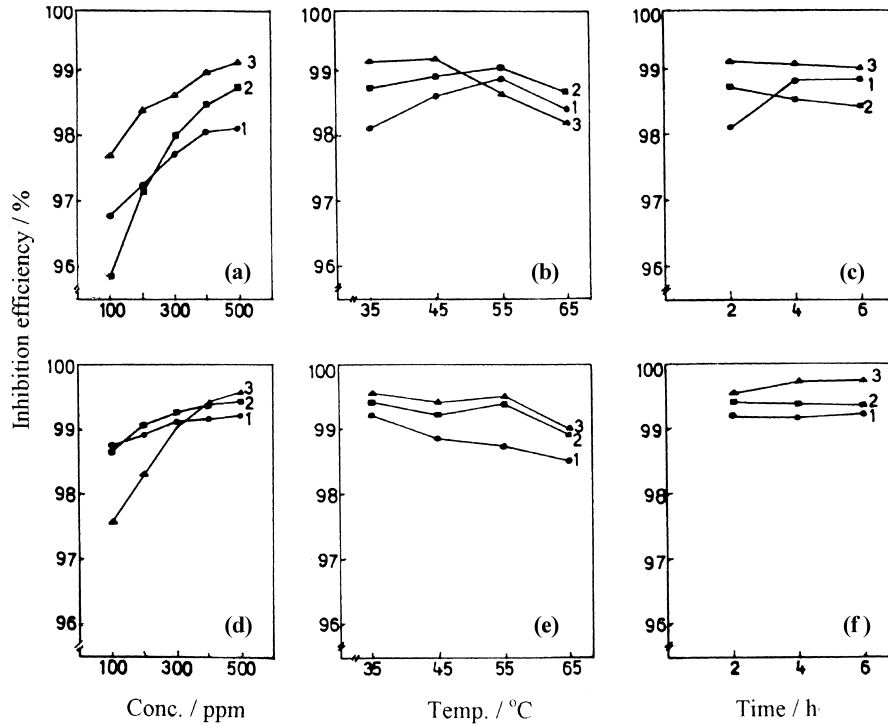
Fig. 1. Variation of inhibition efficiency with: (a) inhibitor concentration, (b) solution temperature, (c) immersion time, in 1 M HCl and (d) inhibitor concentration, (e) solution temperature, (f) immersion time, in 0.5 M H₂SO₄ (1, PUTT; 2, HPTT; 3, DPTT).

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

$$\ln\left(\frac{r_2}{r_1}\right) = -\frac{E_a \Delta T}{R T_1 T_2} \qquad (3)$$

where r_1 and r_2 are corrosion rates at temperatures T_1 and T_2, respectively, and $\Delta T = T_2 - T_1$. The free energy of adsorption (ΔG_{ads}) at different temperatures were calculated from using Equation 4 [19]:

$$\Delta G_{ads} = -RT \ln\left(55.5\, K\right) \qquad (4)$$

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) and K is the equilibrium constant. The values of E_a and ΔG_{ads} are given in Table 2. It is found that E_a values for inhibited systems are higher than that of uninhibited

systems except for PUTT in 1 M HCl, indicating that all the inhibitors except PUTT in 1 M HCl are more effective at room temperature. The E_a value for PUTT is less than E_a for 1 M HCl alone, and hence exhibit high e_{IE} at elevated temperatures [20]. The negative values of free energy of adsorption indicate spontaneous adsorption of the inhibitors on the mild steel surface [21]. The values ΔG_{ads} for all the compounds at higher temperatures are more than 40 kJ mol⁻¹ indicating that the inhibitor molecules are chemisorbed [22]. The negative values of ΔG_{ads} also suggest the strong interaction of the inhibitor molecules on the mild steel surface [23].

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 [24]. The surface

Table 2. Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 1 M HCl and 0.5 M H₂SO₄ in the absence and presence of 500 ppm concentration of various inhibitors

System	E_a/kJ mol⁻¹	$-\Delta G_{ads}$/kJ mol⁻¹			
		35 °C	45 °C	55 °C	65 °C
1 M HCl	47.27	–	–	–	–
PUTT	44.01	37.45	39.50	41.04	41.80
HPTT	50.20	37.95	39.54	41.17	41.46
DPTT	68.92	38.79	40.21	40.00	40.46
0.5 M H₂SO₄	46.81	–	–	–	–
PUTT	65.58	39.75	40.04	41.04	41.80
HPTT	67.42	40.04	40.54	42.46	42.05
DPTT	74.40	40.58	41.17	43.05	42.21

coverage values (θ) were evaluated using corrosion rate values (r) obtained from the weight loss method. The θ values for different concentrations of inhibitors were tested graphically by fitting to various isotherms. A plot of $\log \theta/(1-\theta)$ against $\log C$ for different concentrations shows a straight line indicating that adsorption from both acids follows the Langmuir adsorption isotherm (Figure 2(a) and (b)) [25].

3.3. Potentiodynamic polarization

Potentiodynamic anodic and cathodic polarization scans were carried out in 1 M HCl and 0.5 M H$_2$SO$_4$ for different fatty acid triazoles at 28 $\pm$ 2 °C. The various electrochemical parameters calculated from Tafel plots are given in Table 3. The lower corrosion current density (I_{corr}) values in the presence of the

Fig. 2. Langmuir adsorption isotherm plots for the adsorption of various inhibitors in: (a) 1 M HCl and (b) 0.5 M H$_2$SO$_4$, on the surface of mild steel (1, PUTT; 2, HPTT; 3, DPTT).

triazoles without causing significant changes in corrosion potential (E_{corr}) suggest that the compounds are mixed type inhibitors (i.e., inhibit both the anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction. The maximum decrease in the I_{corr} value was observed for DPTT (5-Dec-9-enyl-4-phenyl-4H- [1,2,4] triazole-3-thiol) indicating that DPTT is the most effective corrosion inhibitor among the studied fatty acid triazoles.

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 3(a) and (b). The impedance diagrams are not perfect semicircles and this difference has been attributed to frequency dispersion [26]. The values of R_t and C_{dl} were obtained using the Nyquist and Bode plots, respectively [27]. The percentage e_{IE} was calculated using Equation 5:

$$e_{IE} = \frac{(1/R_{t0}) - (1 - R_{ti})}{(1/R_{t0})} \times 100 \qquad (5)$$

where R_{t0} and R_{ti} are charge transfer resistance without and with inhibitor, respectively, and is given in Table 4. Values of R_t increase with increase in inhibitor concentration (DPTT) and this in turn leads to an increase in the inhibition efficiency. The addition of DPTT to 1 M HCl lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor [28].

3.5. Auger electron spectroscopy

Auger electron spectroscopy for mild steel exposed to 500 ppm of DPTT is shown in Figure 4. The appearance of peaks at 152 and 380 eV confirm the adsorption of DPTT to the mild steel surface through the S- and N-atoms [29].

3.6. Mechanism of corrosion inhibition

The effectiveness of a compound as corrosion inhibitor depends on its structure. Inhibition of corrosion of mild steel in the acidic solution by the fatty acid triazoles can be explained on the basis of molecular adsorption. It is apparent from the molecular structure that the compounds are able to adsorb on the metal surface through the lone pair of electrons of N-, O- and S-atoms, the π-electrons of the benzene ring and as a protonated species [30]. The cationic species may adsorb on the cathodic sites of the mild steel and reduce the evolution of hydrogen. The highest inhibition efficiency exhibited by DPTT may be attributed to its adsorption on the metal surface through polar groups, as well as through the π-electrons of the double bond. This leads to greater surface coverage, thereby giving higher inhibition efficiency. PUTT showed lowest inhibition efficiency due to
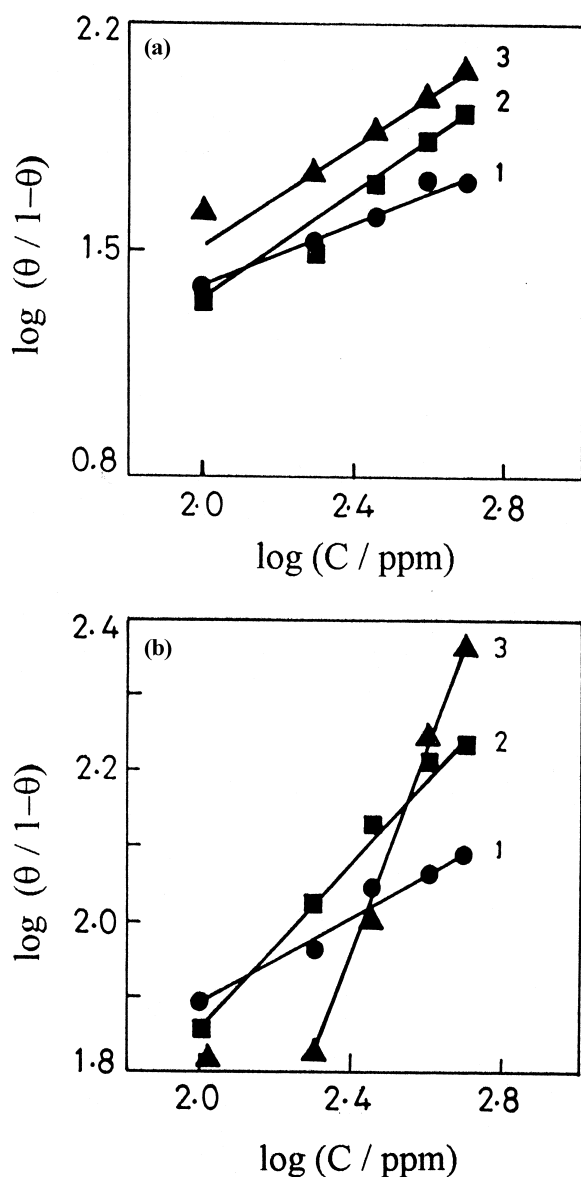
Table 3. Electrochemical polarization parameters for the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 in the absence and presence of 500 ppm concentration of various inhibitors

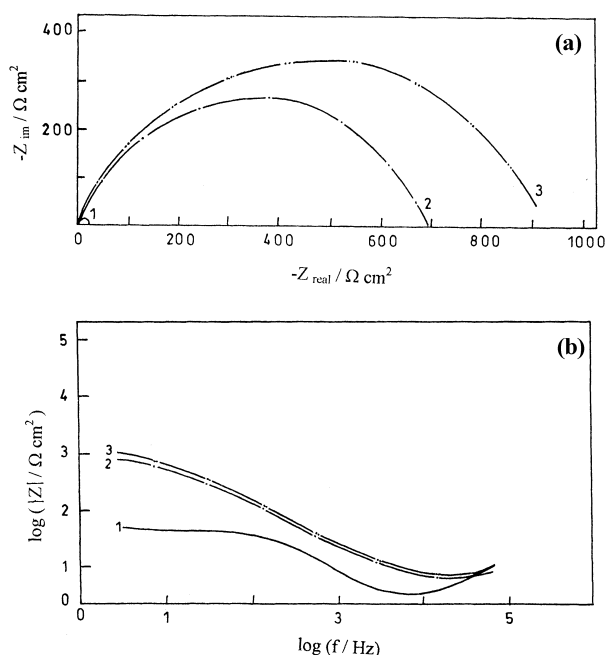| System	1 M HCl			0.5 M H_2SO_4		
	E_{corr} /mV	I_{corr} /mA cm^{-2}	e_{IE} /%	E_{corr} /mV	I_{corr} /mA cm^{-2}	e_{IE} /%
Blank	−596	0.350	−	−568	0.37	−
PUTT	−596	0.054	84.57	−572	0.024	93.51
HPTT	−600	0.047	86.57	−563	0.016	95.67
DPTT	−618	0.042	88.00	−563	0.013	96.48

Fig. 3. (a) Nyquist plot and (b) Bode plot for mild steel in absence and presence of various concentrations of DPTT (1, 1 M HCl; 2, 100 ppm and 3, 500 ppm).
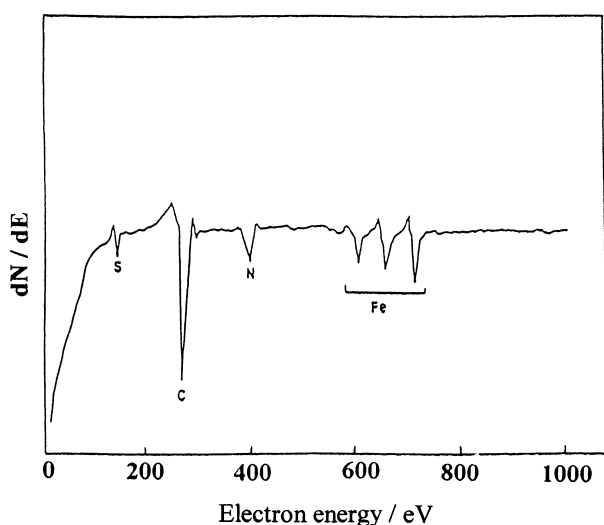

Fig. 4. Auger electron spectrum for mild steel surface exposed to 1 M HCl containing DPTT.

Table 4. Electrochemical impedance parameter for mild steel in 1 M HCl containing different concentrations of DPTT at room temperature

Concentration /ppm	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	e_{IE} /%
1 M HCl DPTT	18.02	1412.63	−
100	664.4	74.99	97.29
500	928.3	55.98	98.06

the absence of a double bond in the hydrocarbon chain. HPTT, containing an internal double bond at position 8, showed less inhibition efficiency than DPTT, containing a π–bond and 10 carbon atoms, because compounds containing more than 10 carbon atoms show a lower inhibition efficiency owing to decreased solubility and increased steric hindrance to adsorption [31]. The ΔG_{ads} values also corroborate the adsorption mechanism.

4. Conclusions

The main conclusions concerning, fatty acid triazoles are that (i) they show excellent performance as corrosion inhibitors in both hydrochloric and sulfuric acid media; and (ii) 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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