

Inhibition of mild steel corrosion in formic and acetic acid solutions

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Four organic inhibitors namely, 4-amino-3-methyl-5-mercapto-1,2,4-triazole (AMMT), 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (AEMT), 4-amino-3-propyl-5-mercapto-1,2,4-triazole (APMT) and 4-amino-3-butyl-5-mercapto-1,2,4-triazole (ABMT) were synthesized to investigate their inhibiting actions on corrosion of mild steel (MS) in aqueous solutions containing 20% formic acid and 20% acetic acid by weight loss and potentiodynamic polarization methods. All of these compounds have shown good inhibition efficiency (*IE*) in the formic acid and acetic acid solutions. *IE* of these compounds has been found to vary with the concentration of the compounds, temperature, immersion time and concentration of acid solutions. The adsorption of these compounds on the mild steel surface from both the acids has been found to obey Langmuir adsorption isotherm. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) indicated physical adsorption of these compounds on the steel surface. The potentiodynamic polarization experiments revealed that all the compounds are mixed type inhibitors.

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Corrosion behaviour of iron and mild steel in organic acid solutions has attracted the attention of several investigators¹⁻³. Corrosion studies on metals in organic acid solutions are scarce in comparison with similar studies in mineral acids⁴⁻⁷. Mild steel is used for fabrication of reaction vessels, storage tanks etc. by industries, which either manufacture or use organic acids as reactant. Organic acid ranks among the most important chemicals in industry today. The reactive carboxyl group –COOH makes them a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibers.

Here the influence of four triazoles namely, 4-amino-3-methyl-5-mercapto-1,2,4-triazole (AMMT), 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (AEMT), 4-amino-3-propyl-5-mercapto-1,2,4-triazole (APMT) and 4-amino-3-butyl-5-mercapto-1,2,4-triazole (ABMT) on corrosion of mild steel in aqueous solutions containing 20% formic acid and 20% acetic acid is reported. The selection of these inhibitors is based on the considerations such as (a) these can be synthesized conveniently from relatively cheap raw materials, (b) compounds contain nitrogen with, presence of non-bonding electron pairs and (c) readily

polarizable sulphur atoms in the compounds are, likely to induce greater adsorption of the compounds on the metal surface leading to higher efficiency.

Experimental Procedure

Inhibitors

The inhibitors were synthesized in the laboratory following the procedure described earlier⁸ and compounds were characterized through their spectral data and their purity was confirmed by thin layer chromatography (TLC). Name and structural formula of the inhibitors examined are given in Table 1.

Electrolyte

Analytical grade formic acid, acetic acid and double distilled water were used for preparing test solutions for all the experiments. All the experiments were carried in 20% formic and 20% acetic acid solutions.

Specimens

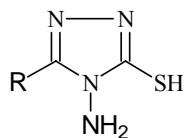
The mild steel samples having composition, (wt %): 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and balance Fe were used for the experiment.

Weight loss studies

Weight loss studies were performed in accordance with ASTM methods⁹⁻¹⁰. Tests were conducted in 20% formic acid and 20% acetic acid solutions for 24 h at 30°C with 50, 100, 200, 300, 400 and 500 ppm

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Table 1 — Name and molecular structures of the compounds used



- 1 R=CH₃ (4-Amino-3-methyl-5-mercapto-1,2,4-triazole, AMMT)
- 2 R=C₂H₅ (4-Amino-3-ethyl-5-mercapto-1,2,4-triazole, AEMT)
- 3 R=C₃H₇ (4-Amino-3-propyl-5-mercapto-1,2,4-triazole, APMT)
- 4 R=C₄H₉ (4-Amino-3-butyl-5-mercapto-1,2,4-triazole, ABMT)

concentrations of inhibitors, in 20% formic acid and 20% acetic acid containing 500 ppm of each inhibitor at different immersion times, at three temperatures ranging from 30, 40 and 50°C for 24 h, and in 10, 20 and 30% formic and acetic acid containing 500 ppm of each inhibitor at 30°C for 24 h.

Electrochemical polarization measurement

For potentiodynamic polarization studies, mild steel strips of same composition, coated with commercially available lacquer (lakme) with an exposed area of 1.0 cm² were used and the experiments were carried out in 20% formic and acetic acid solutions at temperature (26 ± 2°C) with 500 ppm of each inhibitor. Equilibrium time leading to steady state of the specimens was 30 min. Sweep rate in potentiodynamic experiment was 1 mV/s. Potentiodynamic polarization studies were carried out using an EG & G Princeton Applied Research (PAR) potentiostat/galvanostat (model 173), a universal programmer (model 175) and a X-Y recorder (model RE0089). A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) was used as reference electrode.

Results and Discussion

Weight loss studies

The values of percentage inhibition efficiency (*IE*) and corrosion rate (*CR*) obtained from weight loss studies are given in Tables 2 and 3. It is seen that all of these compounds inhibit corrosion of mild steel in 20% formic acid and 20% acetic acid at all concentrations under study. It has been observed that *IE* for all these compounds increases with increase in concentration (Figs 1a & 2a). Maximum inhibition efficiency of each compound within the range of chosen concentration was achieved at 500 ppm and a

Table 2 — Corrosion parameters for mild steel in aqueous solution of 20% formic acid in the absence and presence of different concentrations of various inhibitors from weight loss measurements at 30 °C for 24 h

Inhibitor concentration (ppm)	Initial weight of specimen (g)	Final weight of specimen (g)	CR (mmpy)
20% Formic acid			
Blank	0.9499	0.6388	14.45
AMMT			
50	0.9365	0.9012	1.64
100	0.9383	0.9121	1.22
200	0.9132	0.8931	0.93
300	0.9444	0.9252	0.89
400	0.8831	0.8676	0.72
500	0.9328	0.9216	0.52
AEMT			
50	0.9391	0.9112	1.30
100	0.9204	0.8972	1.08
200	0.9055	0.8856	0.92
300	0.8087	0.7912	0.81
400	0.9658	0.9526	0.61
500	0.9913	0.9812	0.47
APMT			
50	0.9905	0.9712	0.90
100	0.9302	0.9127	0.81
200	0.9709	0.9576	0.62
300	0.8745	0.8626	0.55
400	0.9021	0.8929	0.43
500	0.8701	0.8626	0.35
ABMT			
50	0.8127	0.7999	0.59
100	0.8771	0.8662	0.51
200	0.9816	0.9727	0.41
300	0.9752	0.9672	0.37
400	0.9875	0.9812	0.29
500	0.9013	0.8962	0.24

further increase in concentration did not show any appreciable change in the performance of the inhibitor.

The influence of temperature on *IE* at 500 ppm of each inhibitor is shown in Figs 1b and 2b. It is

Table 3 — Corrosion parameters for mild steel in aqueous solution of 20% acetic acid in the absence and presence of different concentrations of various inhibitors from weight loss measurements at 30 °C for 24 h

Inhibitor concentration (ppm)	Initial weight of specimen (g)	Final weight of specimen (g)	CR (mmpy)
20% Acetic acid			
Blank	0.9538	0.8020	7.05
AMMT			
50	0.9528	0.9256	1.26
100	0.9350	0.9121	1.06
200	0.9949	0.9777	0.80
300	0.9974	0.9812	0.75
400	0.9849	0.9712	0.60
500	0.9943	0.9812	0.61
AEMT			
50	0.9477	0.9276	0.93
100	0.9211	0.9012	0.92
200	0.8815	0.8662	0.71
300	0.9111	0.8992	0.55
400	0.8099	0.7994	0.49
500	0.9068	0.8976	0.43
APMT			
50	0.8727	0.8556	0.79
100	0.9145	0.8992	0.71
200	0.9996	0.9871	0.58
300	0.8025	0.7921	0.48
400	0.8793	0.8692	0.47
500	0.9306	0.9216	0.42
ABMT			
50	0.9094	0.8992	0.47
100	0.9899	0.9812	0.40
200	0.9829	0.9767	0.29
300	0.9290	0.9237	0.25
400	0.9864	0.9815	0.23
500	0.9260	0.9216	0.20

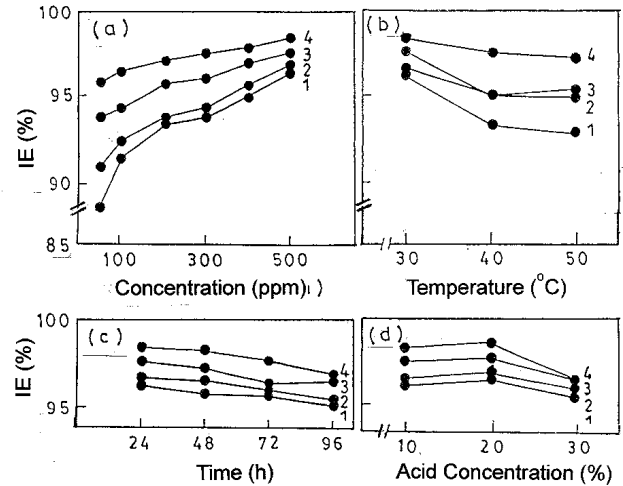


Fig. 1a — Variation of inhibition efficiency with inhibitor concentration in 20% formic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)
 Fig. 1b — Variation of inhibition efficiency with solution temperature in 20% formic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)
 Fig. 1c — Variation of inhibition efficiency with immersion time in 20% formic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)
 Fig. 1d — Variation of inhibition efficiency with different acid concentrations (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

observed that the *IE* decreases with increase in temperature from 30 to 50°C. The decrease of *IE* with temperature is attributed to desorption of the inhibitor molecules from metal surface at higher temperatures¹¹. Figs 1c and 2c show the variation of the *IE* at 500 ppm with immersion time. It is observed that the *IE* of all the compounds decreases as on increasing immersion time from 24 to 96 h.

The effect of acid concentration of formic and acetic acid for 24 h of exposure at 500 ppm of all the compounds on *IE* is shown in Figs 1d and 2d. It is found that with increase in concentration of formic acid and acetic acid the *IE* initially increases and attains a maximum value at 20% concentration of acid and decreases on further increase in the acid concentration to 30%.

The values of activation energy (*E_a*) were calculated using the Arrhenius equation¹²⁻¹³,

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

where *r₁* and *r₂* are the corrosion rates at temperatures *T₁* and *T₂*, respectively, and $\Delta T = T_1 - T_2$. The free energy of adsorption (ΔG_{ads}) at different temperatures were calculated using following equation¹⁴,

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

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) and K is the equilibrium constant. The value of E_a and ΔG_{ads} are given in Table 4. The low and negative values of free energy of adsorption indicate spontaneous adsorption of inhibitors on the mild steel surface. The negative value of ΔG_{ads} also suggest the strong interaction of the inhibitor molecules with the mild steel surface¹⁵⁻¹⁶. It was found that E_a was higher in the presence of inhibitors indicating that these inhibitors are more effective at lower temperature¹⁷.

Application of adsorption isotherm

The surface coverage values (θ) were evaluated using corrosion rate values (CR) obtained from weight loss method. 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 (Figs 3a & b).

Potentiodynamic polarization studies

The polarization behaviour of mild steel in 20% formic acid and 20% acetic acid in the absence and

Table 4 — Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 20% formic acid and 20% acetic acid in the absence and presence of maximal concentration of the inhibitor

Inhibitor concentration (500 ppm)	E_a (k.cal.mol ⁻¹)	$-\Delta G_{ads}$ (k.cal.mol ⁻¹)		
		30°C	40°C	50°C
20% Formic acid	12.05	-	-	-
AMMT	19.35	7.76	7.62	7.82
AEMT	16.03	7.88	7.88	8.12
APMT	18.44	8.12	7.49	8.20
ABMT	16.31	8.41	8.45	8.66
20% Acetic acid	6.34	-	-	-
AMMT	7.42	7.20	7.41	7.59
AEMT	6.34	7.49	7.63	7.73
APMT	8.64	7.56	7.69	7.89
ABMT	10.29	8.06	8.10	8.33

presence of 500 ppm inhibitor concentration is shown in Figs (4a & b). Electrochemical parameters such as corrosion current density (I_{corr}) and corrosion potential (E_{corr}) calculated from Tafel plots are given in Table 5.

The maximum decrease in I_{corr} was observed at 500 ppm concentration for each of these compounds. Maximum decrease in I_{corr} was observed for ABMT indicating that ABMT is most effective corrosion inhibitor. Similar trend was observed in weight-loss method. E_{corr} values do not show any significant change in the presence of all the compounds suggesting that all these compounds are mixed type inhibitors.

The inhibition of corrosion of mild steel in the acids by the triazoles can be explained on the basis of adsorption. In acidic solutions, the triazoles investigated can exist as cationic species like amines¹⁸. The cationic species possess positive charge so they are adsorbed on the cathodic sites of the mild steel as it carries negative charge. While the

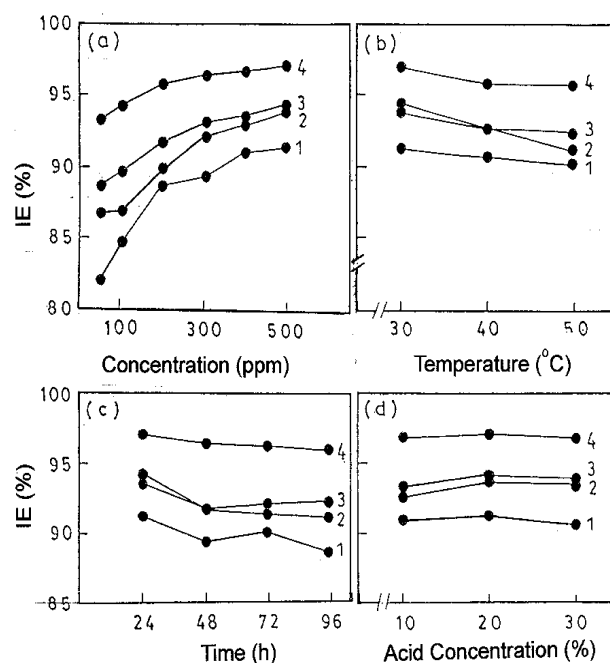


Fig. 2a — Variation of inhibition efficiency with inhibitor concentration in 20% acetic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 2b — Variation of inhibition efficiency with solution temperature in 20% acetic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 2c — Variation of inhibition efficiency with immersion time in 20% acetic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 2d — Variation of inhibition efficiency with different acid concentrations (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 2d — Variation of inhibition efficiency with different acid concentrations (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

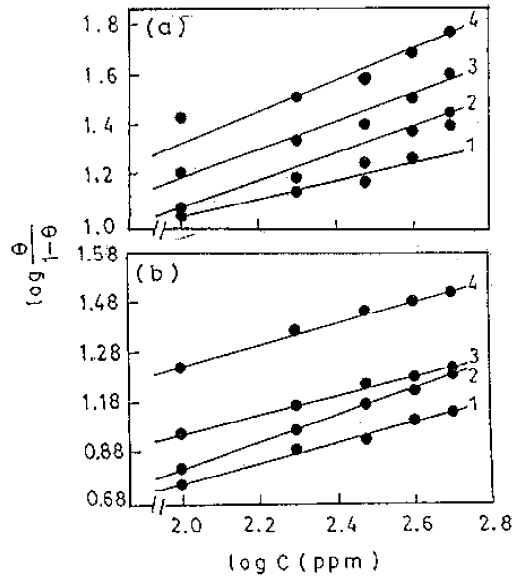


Fig. 3a — Langmuir adsorption isotherm plots for the adsorption of inhibition in 20% formic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 3b — Langmuir adsorption isotherm plots for the adsorption of inhibition in 20% acetic acid (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

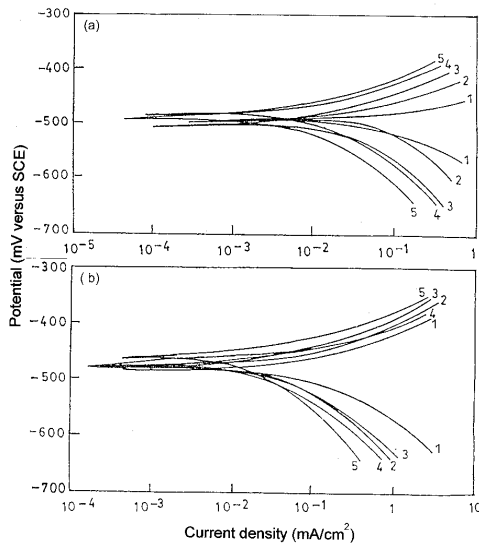


Fig. 4a — Typical potentiodynamic curves for MS in 20% formic acid in the presence and absence of inhibitor containing 500 ppm concentration (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

Fig. 4b — Typical potentiodynamic curves for MS in 20% acetic acid in the presence and absence of inhibitor containing 500 ppm concentration (1, AMMT; 2, AEMT; 3, APMT; 4, ABMT)

adsorption of these compounds at anodic sites takes place through lone pair of electrons of N and S atoms and π -electrons of the triazole ring which reduces the anodic dissolution of mild steel.

Table 5 — Electrochemical polarization parameters for the corrosion of mild steel in 20% formic acid and 20% acetic acid containing maximal concentration of various inhibitors at $26 \pm 2^\circ\text{C}$

Inhibitor concentration (500 ppm)	E_{corr} (mV)	I_{corr} (mA cm^{-2})	IE (%)
20% Formic acid	-498	0.25	-
AMMT	-500	0.061	75.6
AEMT	-508	0.034	86.4
APMT	-490	0.025	90.0
ABMT	-495	0.013	94.8
20% Acetic acid	-492	0.14	-
AMMT	-490	0.041	70.7
AEMT	-484	0.032	77.1
APMT	-484	0.025	82.1
ABMT	-478	0.019	86.4

Conclusion

Thus, it may be concluded that,

- (i) All investigated triazoles behaved as good corrosion inhibitors in 20% formic acid and 20% acetic acid.
- (ii) They inhibited the corrosion of mild steel in acid solutions by adsorption mechanism and the adsorption of these compounds on the metal surface obeyed Langmuir adsorption isotherm.
- (iii) All of the compounds behaved as mixed type inhibitors.

References

- 1 Constatinescu E & Heitz E, *Corros Sci*, 16 (1976) 857.
- 2 Sekine I & Chinda A, *Corrosion*, 40 (1984) 95.
- 3 Quraishi M A, Ansari F A & Jamal D, *Mat Chem Phy*, 77 (2002) 687.
- 4 Sekine I A, Masuko A & Senoo K, *Corros Sci*, 43 (1987) 553.
- 5 Quraishi M A & Jamal D, *Corrosion*, 56 (2000) 156.
- 6 Singh V B & Singh R N, *Corros Sci*, 37 (1995) 1399.
- 7 Sekine I, Hatakeyama S & Nakazawa Y, *Corros Sci*, 27 (1987) 275.
- 8 Dhaka K S, Mohan J, Chada V K & Pujari H K, *Indian J Chem*, 12 (1974) 288.

- 9 Mathur P B & Vasudevan T, *Corrosion*, 38 (1982) 17.
- 10 ASTM G 31-72, *Standard Practice for Laboratory Immersion Corrosion Testing of Metals* (West Conshohocken, PA; ASTM), 1990.
- 11 Ajmal M, Jamal D & Quraishi M A, *Anti-Corros Methods Mater*, 47 (2000) 77.
- 12 Schorr M & Yahalom J, *Corros Sci*, 12 (1972) 867.
- 13 Vashi R T & Champaneri V A, *Indian J Chem Technol*, 4 (1997) 180.
- 14 Rodosevic J, Kliskic M, Aljinovic L J & Vuko S, *Proc of 8th European Symposium on Corrosion Inhibition*, Ann Univ. Ferrara, Italy 1995, 917.
- 15 Elachauri M, Hajji M S, Salem M, Kertit S, Aride J, Coudert R & Essasi E, *Corrosion*, 52 (1996) 103.
- 16 Savithri B V & Mayanna S, *Indian J Chem Technol*, 3 (1996) 256.
- 17 Putilova I N, Balezin S A & Baranik U P, *Metal Corrosion Inhibitors* (New York, NY: Pergamon Press), 1960, 31.
- 18 Banerjee G & Malhotra S N, *Corrosion*, 48 (1992) 14.