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Thiazoles as corrosion inhibitors for mild steel in formic and acetic acid solutions

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Abstract

2-(*N*,*N*-dimethylamino) benzylidene imino-4-(4-methyl phenyl)-1,3-thiazole (DIMPT), 2-benzylidene imino-4-(4-methyl phenyl)-1,3-thiazole (BIMPT), 2-salicylidene imino-4-(4-methyl phenyl)-1,3-thiazole (SIMPT) and 2-cinnamylidene imino-4-(4-methyl phenyl)-1,3-thiazole (CIMPT) were synthesized in the laboratory and their influence on the inhibition of corrosion of mild steel in 20% formic acid and 20% acetic acid was investigated by weight loss and potentiodynamic polarization techniques. The inhibition efficiency of these compounds was found to vary with their nature and concentration, temperature, immersion time and acid concentration. The values of activation energy and free energy of adsorption of the thiazoles were calculated to investigate the mechanism of corrosion inhibition. The adsorption of all the thiazoles on mild steel surface was found to obey Langmuir adsorption isotherm. The potentiodynamic polarization result revealed that the compounds studied are mixed type inhibitors. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition.

1. Introduction

Corrosion studies on metals in organic acid solutions are scarce in comparison with similar studies in mineral acids [1–4]. Mild steel is used in 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.

Despite the importance of organic acids in industry, few corrosion studies of these acids [5–8] have been made. However, at high temperatures, the acids can dissociate, forming more aggressive ions that can cause faster corrosion than might otherwise be expected.

A variety of organic compounds containing heteroatoms such as O, N, S and multiple bonds in their molecule are of particular interest as they give better inhibition efficiency than those containing N or S alone [9–13].

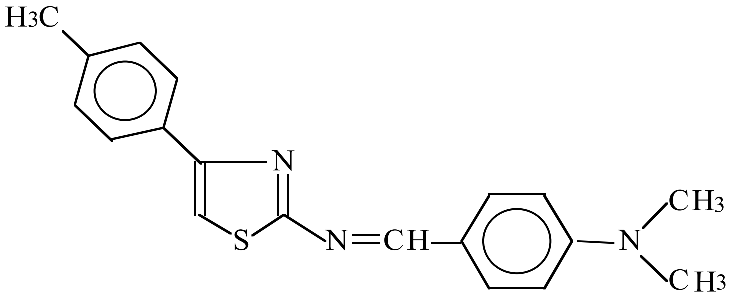
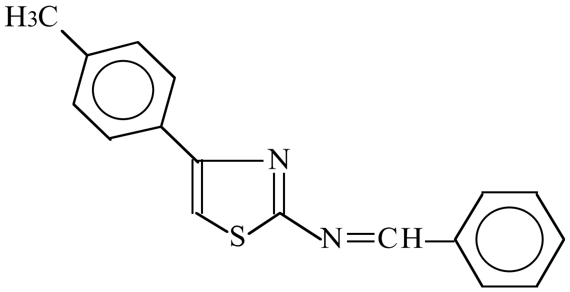
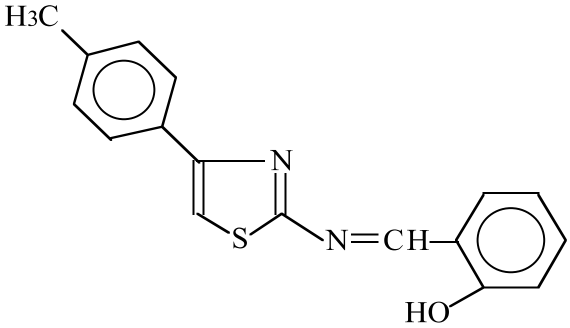
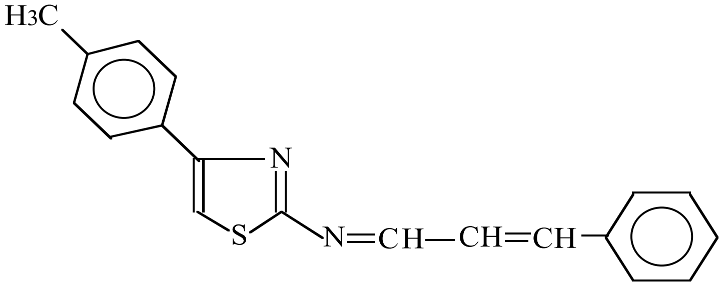
In the present investigation we report the influence of four thiazoles: namely, 2-(*N*,*N*-dimethylamino) benzylidene imino-4-(4-methyl phenyl)-1,3-thiazole (DIMPT), 2-benzylidene imino-4-(4-methyl phenyl)-1,3-thiazole (BIMPT), 2-salicylidene imino-4-(4-methyl phenyl)-1,3-thiazole (SIMPT) and 2-cinnamylidene imino-4-(4-methyl phenyl)-1,3-thiazole (CIMPT) on corrosion inhibition of mild steel in 20% formic acid and 20% acetic acid. The selection of these inhibitors is based on the considerations such as (a) these can be synthesized conveniently from relatively cheap raw materials and (b) compounds contain nitrogen with non-bonding electron pairs additional to the π-electrons of the phenyl and thiazole rings to induce greater adsorption of the compounds on the metal surface leading to higher efficiency.

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, balance Fe as per standard method [14]. The formic acid and acetic acid (Merck) of AR grade were used for preparing solutions. Double distilled water was used to prepare solutions of 20% formic acid and 20% acetic acid. The inhibitors were synthesized in the laboratory following the procedure reported elsewhere [15]. Synthesized compounds were characterized by their infrared spectra and the purity of the compounds were checked by thin layer chromatography. The names and molecular structure 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

Table 1. Name and molecular structure of the compounds

S. no.	Structural formula	Designation and Abbreviation
1.		2-(*N*,*N*-dimethylamino) benzylidene imino-4-(4-methyl phenyl)-1, 3-thiazole (DIMPT)
2.		2-Benzylidene imino-4-(4-methyl phenyl)-1, 3-thiazole (BIMPT)
3.		2-Salicylidene imino-4-(4-methyl phenyl)-1, 3-thiazole (SIMPT)
4.		2-Cinnamylidene imino-4-(4-methyl phenyl)-1, 3-thiazole (CIMPT)

RE0089 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 the working electrode. All the experiments were carried out at constant temperature of 26 ± 2 °C and 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 the mild steel in 20% formic acid at room temperature in the absence and presence of 100 and 300 ppm of CIMPT 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&G PAR (model 5301A) lock-in-amplifier, using an IBM computer.

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

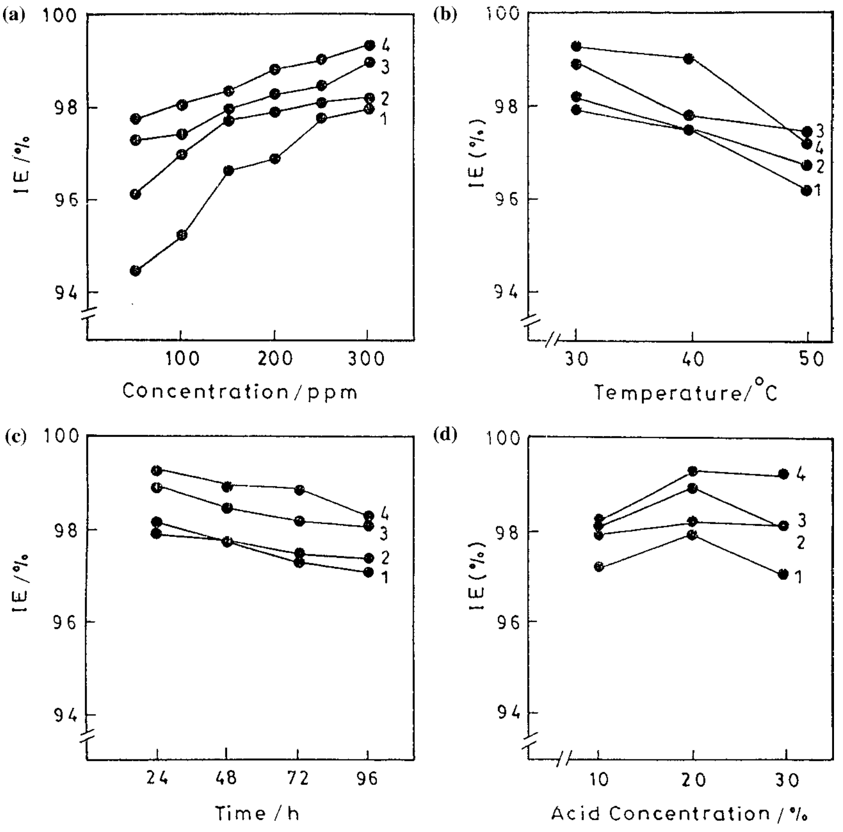


Fig. 1. Variation of inhibition efficiency with: (a) inhibitor concentration (b) solution temperature (c) immersion time and (d) acid concentration, in 20% formic acid (1, DIMPT; 2, BIMPT; 3, SIMPT; 4, CIMPT).

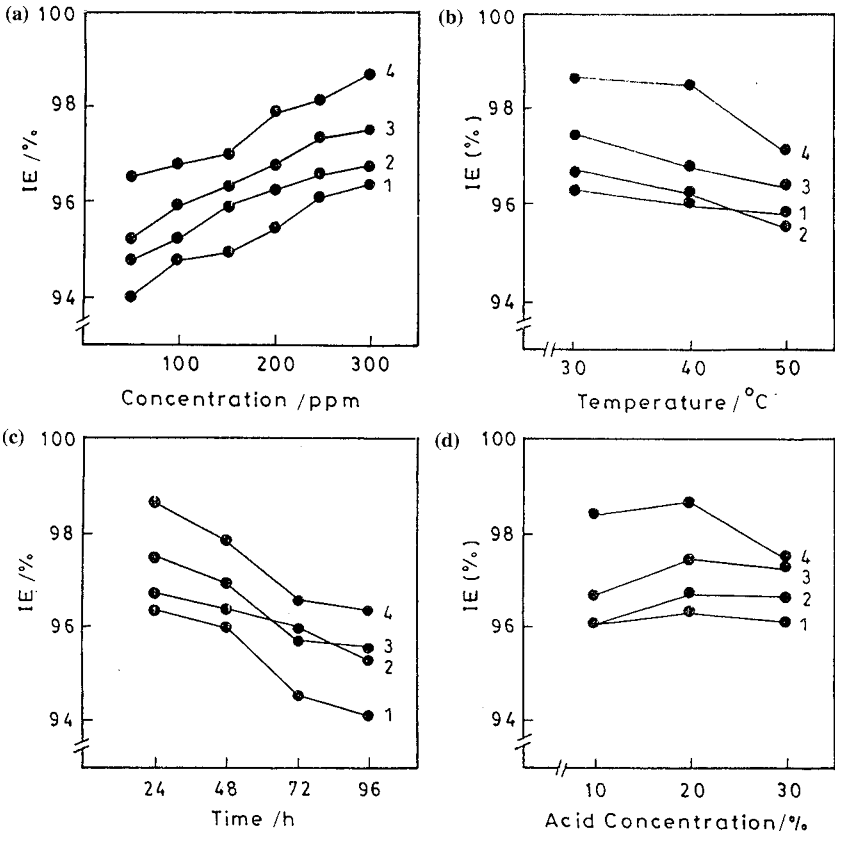


Fig. 2. Variation of inhibition efficiency with: (a) inhibitor concentration (b) solution temperature (c) immersion time and (d) acid concentration, in 20% acetic acid (1, DIMPT; 2, BIMPT; 3, SIMPT; 4, CIMPT).

Table 2. Corrosion parameters for mild steel in 20% formic acid in absence and presence of different concentrations of inhibitor at 30 °C for 24 h from weight loss measurements

Inhibitor Concentraion/ppm	Weight loss/mg	e_{IE}/%	CR/ mm y^{-1}
Blank	311.06	–	14.45
DIMPT			
50	17.2	94.46	0.80
100	14.9	95.22	0.69
150	10.5	96.61	0.49
200	9.7	96.88	0.45
250	6.9	97.78	0.32
300	6.6	97.85	0.31
BIMPT			
50	11.9	96.19	0.55
100	9.6	96.88	0.45
150	7.0	97.72	0.33
200	6.6	97.85	0.31
250	5.9	98.13	0.27
300	5.7	98.20	0.26
SIMPT			
50	8.3	97.30	0.39
100	8.0	97.44	0.37
150	6.5	97.92	0.30
200	5.3	98.27	0.25
250	4.9	98.41	0.23
300	3.2	98.96	0.15
CIMPT			
50	6.9	97.78	0.32
100	6.0	98.06	0.28
150	5.1	98.06	0.24
200	3.5	98.89	0.16
250	3.0	99.03	0.14
300	2.1	99.31	0.10

Table 3. Corrosion parameters for mild steel in 20% acetic acid in absence and presence of different concentrations of inhibitor at 30 °C for 24 h from weight loss measurements

Inhibitor concentraion /ppm	Weight loss/mg	e_{IE}/%	CR/mm y^{-1}
Blank	151.87	–	7.05
DIMPT			
50	9.1	94.04	0.42
100	7.9	94.75	0.37
150	7.5	95.03	0.35
200	6.9	95.46	0.32
250	5.8	96.17	0.27
300	5.5	96.31	0.26
BIMPT			
50	7.9	94.75	0.37
100	7.2	95.32	0.33
150	6.2	95.89	0.29
200	5.7	96.31	0.26
250	5.2	96.59	0.24
300	4.9	96.74	0.23
SIMPT			
50	7.2	95.32	0.33
100	6.1	96.03	0.28
150	5.5	96.31	0.26
200	4.9	96.74	0.23
250	4.0	97.30	0.19
300	3.8	97.45	0.18
CIMPT			
50	5.2	96.59	0.24
100	4.9	96.74	0.23
150	4.7	96.88	0.22
200	3.2	97.87	0.15
250	2.8	98.16	0.13
300	2.0	98.72	0.09

at different thiazole concentrations at 30 °C. The percentage inhibition efficiency (e_{IE}) and surface coverage (θ) of each concentration were calculated using the following 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 inhibitors, respectively. It has been observed that the inhibition efficiency for all the compounds increases with increase in concentrations. The maximum e_{IE} of each compound was achieved at 300 ppm. Schmitt [16] and Quraishi et al. [17] reported that a mixture of nitrogen and sulphur containing compounds are better inhibitors than either type alone. The compounds studied contain both nitrogen and sulphur atoms hence they exhibit good performance on the corrosion of mild steel in 20% formic acid and 20% acetic acid.

The influence of temperature at maximum concentration (i.e., 300 ppm) on e_{IE} is shown in Figures 1(b) and 2(b). The inhibition efficiency for all the thiazoles decreases with increase in temperature from 30 to 50 °C. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperature [18].

The variation of inhibition efficiency with immersion time is shown in Figures 1(c) and 2(c). Inhibition efficiency decreases with increasing the immersion time from 24 to 96 h.

The effect of acid concentration of formic and acetic acid for 24 h of exposure at 300 ppm of all the compounds on e_{IE} is shown in Figures 1(d) and 2(d). It is found that with increase in acid concentration e_{IE} initially increases and attains a maximum value at 20% and decreases on further increase in the acid concentration to 30%.

The values of activation energy (E_a) were calculated using the Arrhenius equation [19, 20]:

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

where, r_1 and r_2 are corrosion rates at temperature T_1 and T_2, respectively, $\Delta T = T_2 - T_1$. The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the equation [21].

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 the inhibitor of 300 ppm of various inhibitors

System	E_a/kJ mol^{-1}	ΔG_{ads} /kJ mol^{-1}		
		30 °C	40 °C	50 °C
20% Formic acid	50.37	–	–	–
DIMPT	74.11	37.37	38.16	38.20
BIMPT	74.61	37.37	37.79	38.25
SIMPT	86.94	33.19	38.29	39.04
CIMPT	108.39	40.13	40.45	38.91
20% Acetic acid	26.45	–	–	–
DIMPT	31.27	35.99	36.91	37.95
BIMPT	39.92	35.91	36.70	37.37
SIMPT	40.71	36.70	37.24	38.12
CIMPT	32.44	38.46	39.33	40.67

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

where $K=\theta$ / C (1− θ), θ is the degree of surface 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 4. E_a values for the inhibited system are higher than these of uninhibited systems, indicating that all the inhibitors are more effective at lower temperatures [22]. The low and negative values of free energy of adsorption (ΔG_{ads}) indicate that spontaneous adsorption of the inhibitor occurs on the mild steel surface [23]. The negative values of ΔG_{ads} also suggest a strong interaction of the inhibitor molecules on the mild steel surface [24].

3.2. *Adsorption isotherm*

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [12]. 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 was linear (Figure 3) suggesting that the adsorption of the compounds on the mild steel surface follows the Langmuir adsorption isotherm which obeys the relation

$$\theta/1-\theta = k\ C\ exp(-\Delta G_{ads}/RT) \tag{5}$$

where ΔG_{ads} is the free energy of adsorption and C is the concentration of inhibitors.

3.3. *Potentiodynamic polarization*

Potentiodynamic anodic and cathodic polarization scans were carried out in 20% formic and acetic acids for different fatty acid triazoles at 26 ± 2 °C. The various electrochemical parameters calculated from Tafel plots are given in Table 5. The lower corrosion current density (I_{corr}) values in the presence of the thiazoles without causing significant changes in corrosion potential (E_{corr}) suggests that they are mixed type inhibitors (Figure 4). The maximum decrease in I_{corr} was observed for CIMPT indicating that this is the most effective corrosion inhibitor among the studied thiazoles.

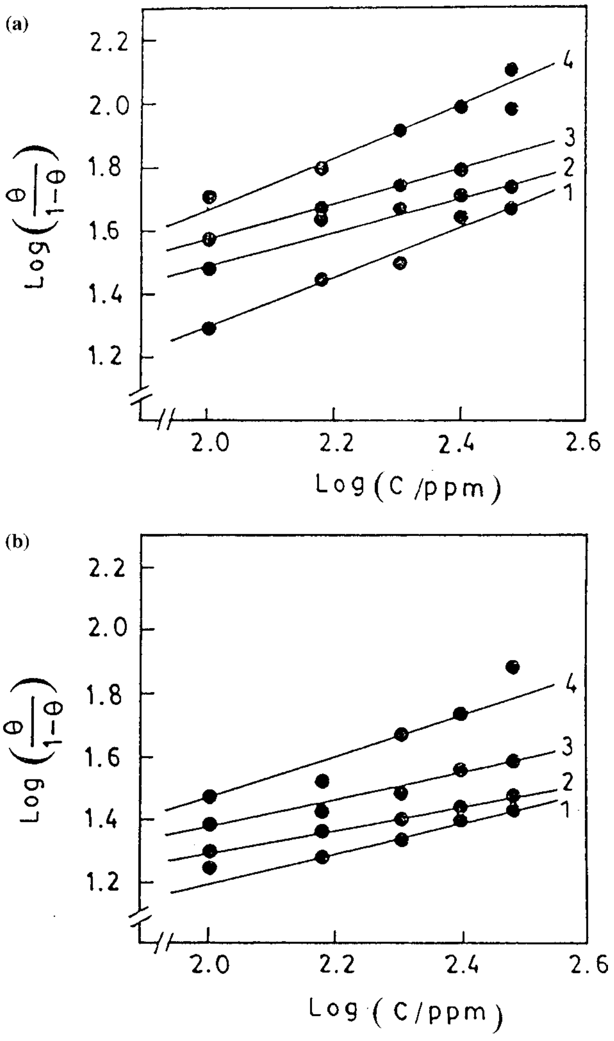


Fig. 3. (a) Langmuir adsorption isotherm plot for the adsorption of various inhibitors in 20% formic acid, on the surface of mild steel (1, DIMPT; 2, BIMPT; 3, SIMPT; 4, CIMPT). (b) Langmuir adsorption isotherm plot for the adsorption of various inhibitors in 20% acetic acid, on the surface of mild steel (1, DIMPT; 2, BIMPT; 3, SIMPT; 4, CIMPT).

3.4. *Electrochemical impedance studies*

The electrical equivalent circuit for the system is shown in Figure 5.

Impedance diagrams obtained for the frequency range 5 Hz–100 kHz at E_{corr} for mild steel in 20% formic acid are shown in Figure 6(a) and (b). The impedance diagrams are not perfect semicircles, and this difference has been attributed to frequency dispersion [25]. The values of charge-transfer resistance (R_t), and double-layer capacitance (C_{dl}) can be evaluated using the Nyquist and Bode plots [26]. e_{IE} was calculated using the equation:

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

Table 5. Electrochemical polarization parameters for the corrosion of mild steel in 20% formic acid and 20% acetic acid in the absence and presence of 300 ppm of various inhibitors

System	E_{corr}/mV	I_{corr}/mA m^{-2}	e_{IE} /%
20% Formic acid	−498	0.25	–
DIMPT	−500	0.014	94.4
BIMPT	−490	0.005	98.0
SIMPT	−496	0.005	98.0
CIMPT	−484	0.0026	98.9
20% Acetic acid	−495	0.14	–
DIMPT	−504	0.035	75.0
BIMPT	−498	0.026	81.4
SIMPT	−494	0.019	86.4
CIMPT	−482	0.018	87.1

where R_{t0} and R_{ti} are the charge-transfer resistance without and with inhibitor, respectively, and are given in Table 6. Values of R_t increases with increase in inhibitor concentration (CIPMT) and this in turn leads to an increase in e_{IE}. The addition of CIPMT to 20% formic acid lowers C_{dl}, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor [27].

3.5. *Mechanism of corrosion inhibition*

Inhibition of corrosion of mild steel in organic acidic solutions by thiazoles 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 of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through π- electrons of aromatic rings and lone pair of electrons of nitrogen and sulphur atoms which may

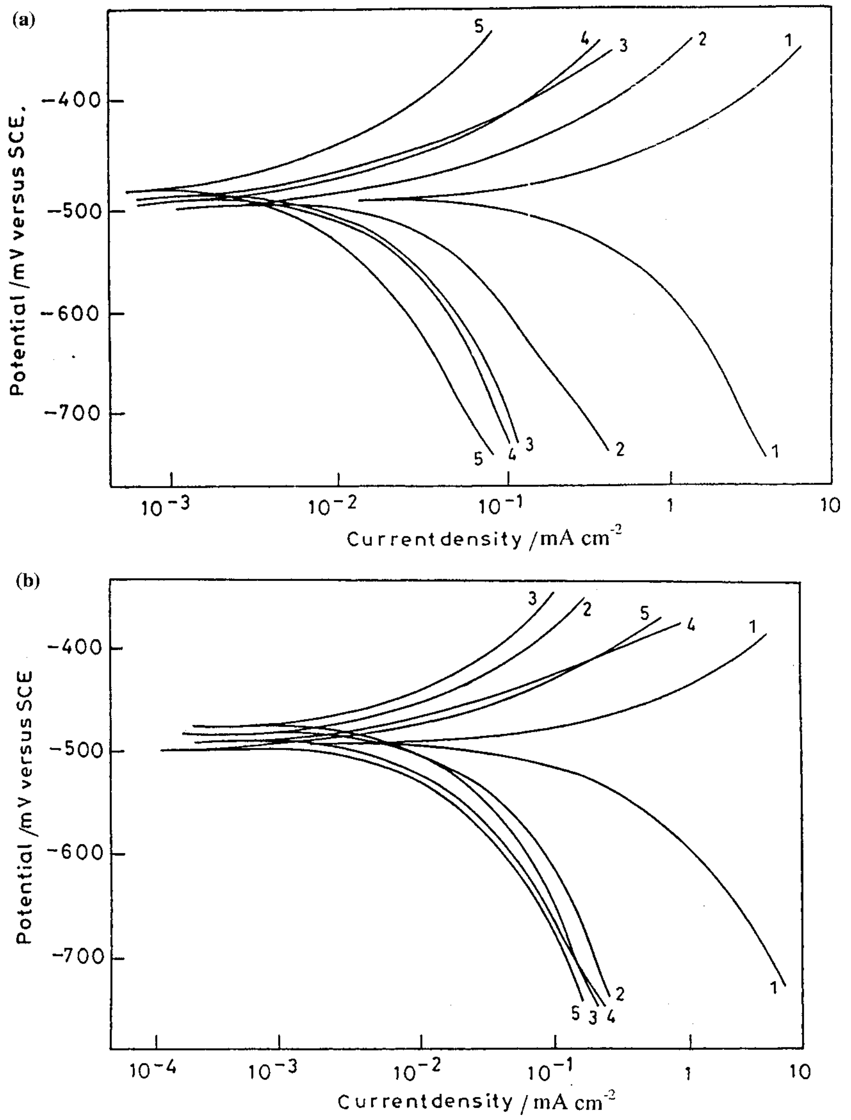


Fig. 4. (a) Electrochemical polarization curves for the corrosion of mild steel in 20% formic acid in the absence and presence of 300 ppm concentration of various inhibitors (1, 20% formic acid; 2, DIMPT; 3, BIMPT; 4, SIMPT; 5, CIMPT). (b) Electrochemical polarization curves for the corrosion of mild steel in 20% formic acid in the absence and presence of 300 ppm concentration of various inhibitors (1, 20% formic acid; 2, DIMPT; 3, BIMPT; 4, SIMPT; 5, CIMPT).

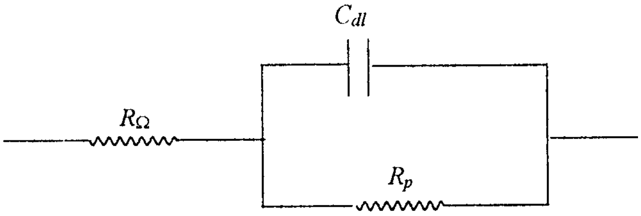


Fig. 5. Electrical equivalent circuit (R_Ω = uncompensated resistance, R_p = polarization resistance,C_{dl} = double layer capacitance.

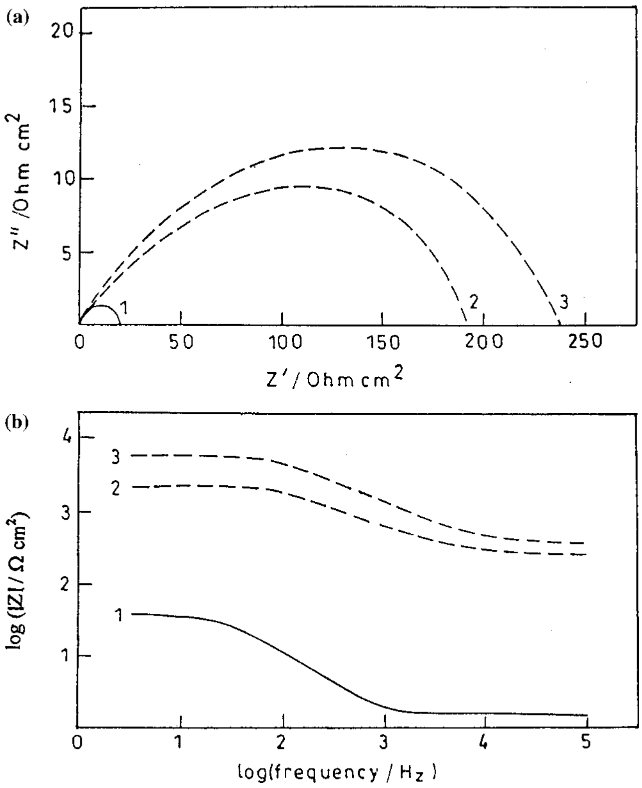


Fig. 6. (a) Nyquist plot and (b) Bode plot for mild steel in the absence and presence of various concentrations of CIMPT (1. Blank; 2. 100 ppm; 3. 300 ppm).

decrease anodic dissolution of mild steel. Among the compounds investigated in the present study, CIMPT has been found to give the best inhibitor performance. This can be explained on the basis of the presence of an additional π- bond between the carbon atoms (–C=C–) in conjugation with azomethine (–N=C=) group. This leads to greater surface coverage, thereby giving higher inhibition efficiency.

Table 6. Electrochemical impedance parameters for mild steel in 20% formic acid containing different concentration of CIMPT

Concentration/ppm	R_t/Ω cm^2	C_{dl}/μ F cm^{-2}	e_{IE}/%
20% Formic acid	15.56	1513.57	–
CIMPT			
100	192.51	79.43	91.75
300	240.00	25.12	93.78

4. Conclusions

- (i) Thiazoles show excellent performance as corrosion inhibitors in 20% formic acid and 20% acetic acid.
- (ii) All the thiazoles acted as efficient corrosion inhibitors over a wide acid range i.e., 10–30% formic acid and acetic acid solutions.
- (iii) They inhibit corrosion of mild steel in 20% formic and 20% acetic acid solutions by an adsorption mechanism which follows the Langmuir adsorption isotherm.

References

1. I.A. Sekine, A. Masuko and K. Senoo, *Corros. Sci.* **43** (1987) 553.
2. M.A. Quraishi and D. Jamal, *Corrosion* **56** (2000) 156.
3. V.B. Singh and R.N. Singh, *Corros. Sci.* **37** (1995) 1399.
4. I. Sekine, S. Hatakeyama and Y. Nakazawa, *Corros. Sci.* **27** (1987) 275.
5. E. Heitz, 'Corrosion of Metals in Organic Solvents', (New York, NY: Plenum Press, 1974), p. 226.
6. I. Sekine, H. Ohkawa, and T. Hank, *Corros. Sci.* **22** (1982) 1113.
7. I. Sekine and A. Chinda, *Corrosion* **40** (1984) 95.
8. M.M. Singh and A. Gupta, *Mat. Chem. Phy.* **46** (1996) 15.
9. S. Muralidharan and S.V.K. Iyer, *Anti-Corros. Met. Mater.* **44** (1997) 100.
10. M.A. Quraishi, M.A.W. Khan and M. Ajmal, *Anti-Corros. Met. Mater.* **43** (1996) 5.
11. B. Hammouti, A. Aouniti, M. Taleb, M. Bright and S. Kertit, *Corrosion* **51** (1995) 411.
12. N. Al-Andis, E. Khamis, A. Al-.Mayouf and H. Aboul-Enein, *Corros. Prev. Cont.* **42** (1995) 13.
13. Abd-El-Nabey, E. Khammis, M.Sh. Ramadan and A. El-Gindy, *Corrosion* **52** (1996) 671.
14. ASTM (American Society for testing and Materials), 'Metal Corrosion, Erosion and Wear', Annual Book of ASTM Standards (1987) 0.3.02, G1–72.
15. M.A. Quraishi, M.W. Khan, M. Ajmal, S. Muralidharan and S.V. Iyer, *Anti-Corros. Met. Mater.* **43** (1996) 5.
16. G. Schmitt, *Brit. Corros. J.* **19** (1984) 165.
17. M.A. Quraishi, M.A. W.Khan, M. Ajmal, S. Muralidharan and S.V. Iyer, *J. Appl. Electrochem.* **26** (1996) 1253.
18. M. Ajmal, D. Jamal and M. A. Quraishi, *Anti-Corros. Met. Mater.* **47** (2000) 77.
19. M. Schorr and J. Yahalom, *Corros. Sci.* **12** (1972) 867.
20. R.T. Vashi and V.A. Champaneri, *Ind. J. Chem. Technol.* **4** (1997) 180.
21. J. Radosevic, M. Kliskic, L.J. Aljinovic and S. Vuko, Proceedings of the 8th European Symposium on 'Corrosion Inhibition', Ann. Univ. Ferrara, Italy (1995), p. 817.
22. I.N. Putilova, S.A. Balezin and U.P. Baranik, 'Metal Corrosion Inhibitors', (New York, NY: Pergamon Press, 1960) p. 31.
23. G.K. Gomma and M.H. Wahadan, *Ind. J. Chem. Technol.* **2** (1995) 107.
24. M. El Achouri, M.S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert and E. Essassi, *Corrosion* **52** (1996) 103.
25. S. Muralidharan, K.L.N. Phani, S. Ravichandran and S.V.K. Iyer, *J. Electrochem. Soc.* (USA), **142** (1995) 1478.
26. S.T. Hirozawa, Proc. 8th Eur. Symp. Corros. Inhib. Ann. University, Ferrara, Italy, **1** (1995) 25.
27. M.A. Quraishi, J. Rawat and M. Ajmal, *Corrosion* **54** (1998) 996.