



Corrosion inhibition by fatty acid triazoles for mild steel in formic acid

M.A. QURAIISHI* and F.A. ANSARI

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh – 202 002, (U.P.) India

(*author for correspondence, e-mail: maquraishi@rediffmail.com)

Received 25 August 2002; accepted in revised form 28 January 2003

Key words: fatty acid triazoles, formic acid, inhibition, mild steel

Abstract

5-Heptadec-8-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (HPTT), 4-phenyl-5-undecyl-4H-[1,2,4] triazole-3-thiol (PUTT), and 5-dec-9-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (DPTT) were synthesized and their influence on the inhibition of corrosion of mild steel in 20% formic 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 and immersion time. The values of activation energy and free energy of adsorption of the triazoles were calculated to investigate the mechanism of corrosion inhibition. Good inhibition efficiency (>90%) was found even at lower concentration (i.e., 25 ppm) in acid solution. The adsorption on mild steel surfaces was found to obey Temkin's adsorption isotherm. Potentiodynamic polarization results revealed that the compounds studied are mixed type inhibitors. Electrochemical impedance spectroscopy was also used to investigate the mechanism of the corrosion inhibition.

1. Introduction

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 [1–5].

Most research on corrosion inhibition of metals has been done in mineral acids. Despite the importance of organic acids in industry, few corrosion studies involving these acids [6–9] have been made. However, at high temperatures, these acids can dissociate, forming more aggressive ions that can cause faster corrosion than might otherwise be expected. In the fabrication of reaction vessels, storage tanks, etc. mild steel is used in the manufacture and use of formic acid. Formic acid is the most corrosive of the common organic acids. In previous work we have studied the effect of a few fatty acid derivatives on the corrosion inhibition of mild steel in acidic solution [10–12]. In the present investigation we report the influence of three fatty acid triazoles: namely, 5-heptadec-8-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (HPTT), 4-phenyl-5-undecyl-4H-[1,2,4] triazole-3-thiol (PUTT), 5-dec-9-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (DPTT) on the corrosion inhibition of mild steel in 20% formic acid.

These fatty acid triazoles were chosen because they are more environmentally benign, have low toxicity and are more cost effective than petroleum based products. Further, they possess nonbonding electron pairs on the

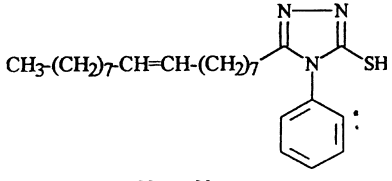
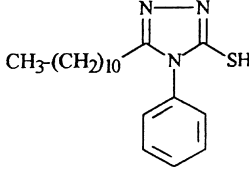
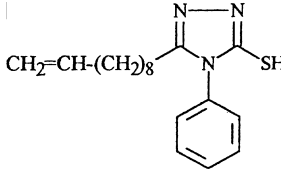
nitrogen atoms additional to the π -electrons of the phenyl and triazole rings and readily polarizable sulfur atoms that tend to induce greater adsorption of the compounds on the metal surface leading to higher efficiency.

2. Experimental details

Weight loss experiments were performed with cold rolled mild steel strips of size 2 cm \times 2.5 cm \times 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 [13]. Formic acid (Merck) of AR grade was used for preparing solutions. Double distilled water was used to prepare 20% solutions. The triazoles of fatty acid were synthesized as described by Kittur et al. [14] and characterized by their infrared spectra and the purities 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 RE0089 X–Y recorder. A platinum foil was used as the auxiliary electrode, a saturated calomel electrode as the reference electrode and mild steel as the working electrode. All the experiments were carried out at a constant temperature of 26 ± 2 °C and a scan rate of

Table 1. Name and structure of fatty acid triazoles used

S. No.	Structure	Designation and abbreviation
1.	 $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$	5-heptadec-8-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (HPTT)
2.	 $\text{CH}_3(\text{CH}_2)_{10}$	4-Phenyl-5-undecyl-4H-[1,2,4] triazole-3-thiol (PUTT)
3.	 $\text{CH}_2=\text{CH}(\text{CH}_2)_8$	5-Dec-9-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol (DPTT)

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 26 ± 2 °C in the absence and presence of 100 and 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&G PAR (model 273A) potentiostat/galvanostat, and an EG&G PAR (model 5301A) lock-in amplifier, using an IBM computer.

3. Results and discussion

3.1. Weight loss

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

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

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

where r_0 and r are the corrosion rates in the absence and presence of inhibitors, respectively. The inhibition efficiency for all the compounds increases with increase in

concentration. The maximum e_{IE} of each compound was achieved at 500 ppm. Schmitt [15] and Quraishi et al. [16] reported that a mixture of nitrogen and sulfur containing compounds are better inhibitors than either type alone. The compounds studied contain both nitrogen and sulphur atoms; hence they exhibit good performance ($e_{\text{IE}} > 94\%$) on the corrosion of mild steel in 20% formic acid, even at low concentration.

The variation of inhibition efficiency with increase in acid concentration is shown in Figure 1(b). It is clear that these compounds are good corrosion inhibitors, providing greater than 90% inhibition efficiency over the acid range from 10% to 30%.

The variation of inhibition efficiency of all the three fatty acid triazoles with immersion time is shown in Figure 1(c). Increase in immersion time from 24 to 96 h show no significant change in inhibition efficiency.

The influence of temperature at maximum concentration (i.e., 500 ppm) on e_{IE} is shown in Figure 1(d). The inhibition efficiency decreases slightly with increase in temperature from 30 to 50 °C, which may be attributed to desorption of the inhibitor molecules from the metal surface at higher temperature.

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

$$\ln\left(\frac{r_2}{r_1}\right) = -\frac{E_a \Delta T}{RT_1 T_2} \quad (3)$$

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 [19].

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

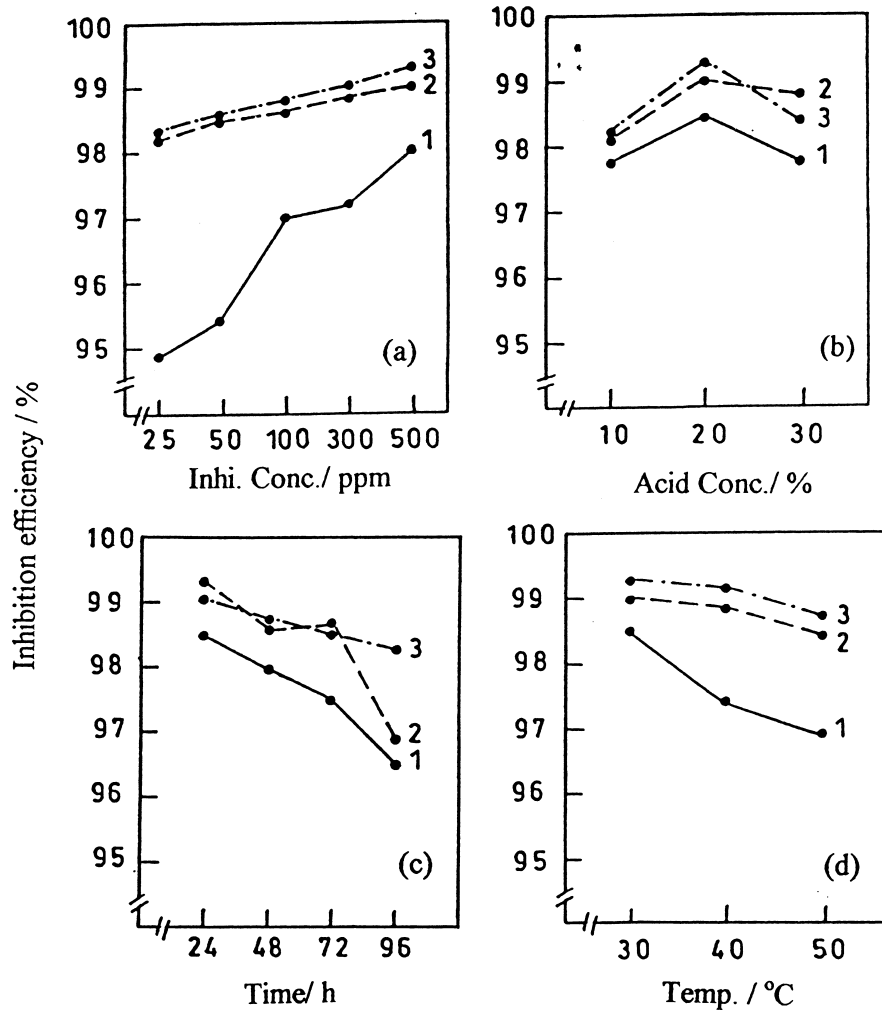


Fig. 1. Variation of inhibition efficiency with: (a) inhibitor concentration, (b) acid concentration, (c) immersion time and (d) solution temperature, in 20% formic acid. (1) HPTT; (2) PUTT; (3) DPTT.

where $K = \theta/C(1 - \theta)$, 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 2. E_a values for inhibited systems are higher than those of uninhibited systems, indicating that all the inhibitors are more effective at room temperature [20]. The low and negative values of free energy of adsorption (ΔG_{ads}) indicate spontaneous adsorption of the inhibitor on the mild steel surface [21]. The values of ΔG_{ads} for all

the compounds are $\leq -40 \text{ kJ mol}^{-1}$ indicating physical adsorption of the inhibitor molecules [22], and the negative values also suggest a strong interaction of the inhibitor molecules on the mild steel surface [23].

3.2. Adsorption isotherm

The mechanism of corrosion inhibition may be explained on the basis of adsorption behaviour [4]. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated by the weight-loss method. Data were tested graphically by fitting to various isotherms. A plot of θ against $\log C$ was linear (Figure 2) suggesting that the adsorption of the compounds on to the mild steel surface follows the Temkin adsorption isotherm. The Temkin isotherm equation is

$$\beta C = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1 - \theta)]} \quad (5)$$

where $\beta = (1/55.5)[\exp - (\Delta G_{\text{ads}}/RT)]$, G_{ads} is the free energy of adsorption, θ the surface coverage, C the

Table 2. Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 20% formic acid in the absence and presence of the inhibitor of 500 ppm of various inhibitors

System	E_a /kJ mol ⁻¹	$-\Delta G_{\text{ads}}$ /kJ mol ⁻¹		
		30 °C	40 °C	50 °C
20% Formic acid	51.28	—	—	—
HPTT	70.48	36.85	37.28	37.99
PUTT	71.32	36.32	38.87	39.25
DPTT	61.44	38.79	39.62	40.42

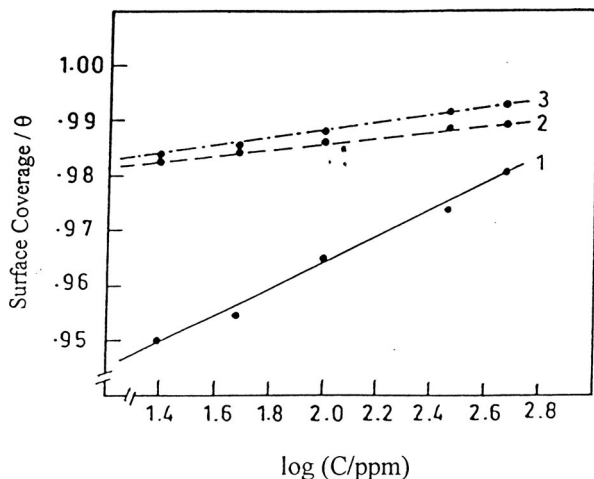


Fig. 2. Temkin's adsorption isotherm plot for the adsorption of various inhibitors in 20% formic acid, on the surface of mild steel. (1) HPTT; (2) PUTT; (3) DPTT.

concentration of inhibitor, a the molecular interaction constant, and for $a > 0$ attraction and for $a < 0 = >$ repulsion.

3.3. Potentiodynamic polarization

Potentiodynamic anodic and cathodic polarization scans were carried out in 20% formic acid for different fatty acid triazoles at 26 ± 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 triazoles, without causing significant changes in corrosion potential (E_{corr}), b_a (anodic Tafel slope) and b_c (cathodic Tafel slope), suggest that they are mixed type inhibitors (Figure 3). The maximum decrease in I_{corr} was observed for DPTT (5-dec-9-enyl-4-phenyl-4H-[1,2,4] triazole-3-thiol).

3.4. Electrochemical impedance

The electrical equivalent circuit for the system is shown in Figure 4. 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 5. The impedance diagrams are not perfect semicircles and this difference has been attributed to frequency dispersion [24]. The values of R_t and C_{dl} were obtained using the Nyquist and Bode plots, respectively [25]. Percentage e_{IE} was calculated using the following:

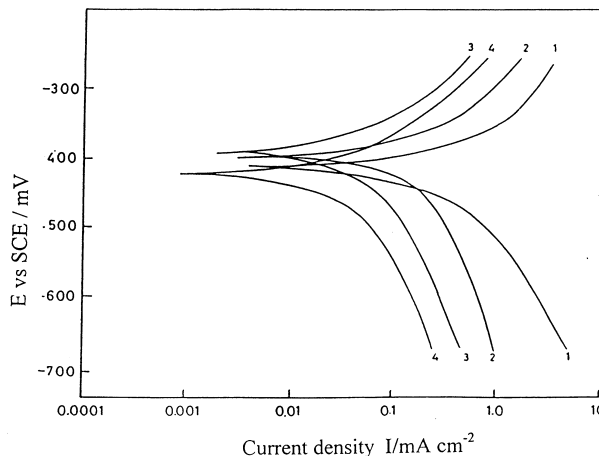


Fig. 3. Electrochemical polarization curves for the corrosion of mild steel in 20% formic acid in the absence and presence of 500 ppm concentration of various inhibitors. (1) 20% formic acid; (2) HPTT; (3) PUTT; (4) DPTT.

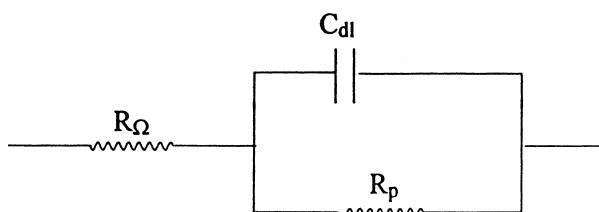


Fig. 4. Electrical equivalent circuit for the system (R_{Ω} uncompensated resistance, R_p polarization resistance and C_{dl} double layer capacitance).

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

where R_{t0} and R_{ti} are the charge transfer resistance without and with inhibitor, respectively, and are given in Table 4. Values of R_t increase with increase in inhibitor concentration (DPTT) and this, in turn, leads to an increase in e_{IE} . The addition of DPTT to 20% formic acid lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption [26].

3.5. Mechanism of corrosion inhibition

The corrosion of mild steel in nonaqueous and aqueous solution may be considered in the following steps [9]:

Table 3. Electrochemical polarization parameters for the corrosion of mild steel in 20% formic acid in the absence and presence of 500 ppm of various inhibitors

System	E_{corr} /mV	b_a /mV decade ⁻¹	b_c /mV decade ⁻¹	I_{corr} /mA cm ⁻²	e_{IE} /%
20% Formic acid	-416	68	104	0.350	–
HPTT	-390	60	120	0.160	54.28
PUTT	-402	70	120	0.062	82.28
DPTT	-420	64	112	0.046	86.85

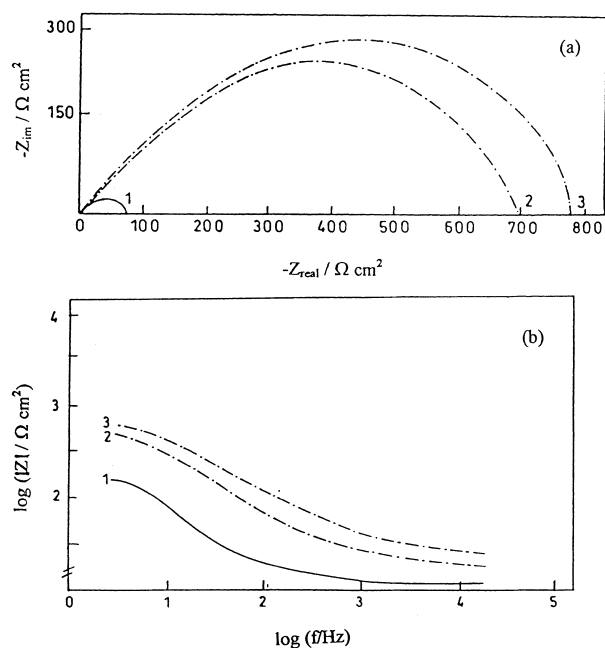
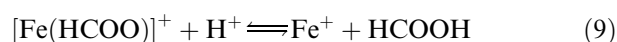


Fig. 5. (a) Nyquist plot and (b) Bode plot for mild steel in the absence and presence of various concentrations of DPTT. (1) 20% formic acid; (2) 100 ppm and (3) 500 ppm.

Table 4. Electrochemical impedance parameters for the corrosion of mild steel in 20% formic acid containing different concentration of DPTT at room temperature

Concentration /ppm	R_t / Ω cm 2	C_{dl} / μ F cm $^{-2}$	ϵ_{IE} /%
20% Formic acid	75.00	1862.09	–
DPTT			
100	700.00	295.80	89.23
500	778.59	258.22	90.15



The evolution of hydrogen occurs as the cathodic reaction by the following mechanism:



The adsorption of formate ions on the surface of iron is a prerequisite for the anodic dissolution to occur; thus the rate of corrosion should depend on the concentration of formate ion in the solution. The conductance of formic acid solution gradually increases in the concentration range 5%–20%. As a result, the extent of adsorption of formate ion, as well as the rate of Step 7 increases and, consequently, the rate of corrosion will also increase.

The triazoles inhibit the corrosion by controlling both the anodic and cathodic reactions. In acidic solutions these 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 the π -electrons of aromatic rings and the lone pair of electrons of nitrogen and sulfur atoms which decrease the anodic dissolution. Among the compounds investigated, DPTT has been found to give the best performance as corrosion inhibitor. This can be explained on the basis of the presence of polar groups, as well as through the π -electrons of the double bond. This leads to greater surface coverage, thereby giving higher inhibition efficiency. HPTT, containing more than 10 carbon atoms in the side chain and an internal double bond at position 8, showed lowest inhibition efficiency, because compounds containing more than 10 carbon atoms have decreased solubility and increased steric hindrance to adsorption [27].

4. Conclusions

Fatty acid triazoles show excellent performance as corrosion inhibitors in formic acid media. All the triazoles acted as efficient corrosion inhibitors over a wide acid range, that is, 10% to 30% formic acid solutions. They inhibit corrosion of mild steel in formic acid by an adsorption mechanism, which follows the Temkin adsorption isotherm.

References

- S. Muralidharan and S.V.K. Iyer, *Anti-Corros Met. and Mater.* **44** (1997) 100.
- M.A. Quraishi, M.A.W. Khan and M. Ajmal, *Anti-Corros. Met. and Mater.* **43** (1996) 5.
- B. Hammouti, A. Aouniti, M. Taleb, M. Bright and S. Kertit, *Corrosion* **51** (1995) 411.
- N. Al-Andis, E. Khamis, A. Al-Mayouf and H. Aboul-Enein, *Corros. Prev. and Cont.* **42** (1995) 13.
- B.A. Abd-El-Nabey, E. Khammis, M.Sh. Ramadan and A. El-Gindy, *Corrosion* **52** (1996) 671.
- E. Heitz, 'Corrosion of Metals in Organic Solvents' (Plenum Press, New York, NY, 1974), p. 226.
- I. Sekine, H. Ohkawa and T. Hank, *Corros. Sci.* **22** (1982) 1113.
- I. Sekine and A. Chinda, *Corrosion* **40** (1984) 95.
- M.M. Singh and A. Gupta, *Mat. Chem. Phys.* **46** (1996) 15.
- M.A. Quraishi, D. Jamal and M.T. Saeed, *J. Am. Oil Chemist's Soc.* **77** (2000) 265.
- M. Ajmal, D. Jamal and M.A. Quraishi, *Anti-Corros. Met. and Mater.* **47** (2000) 77.
- M.A. Quraishi and D. Jamal, *J. Appl. Electrochem.*, submitted.
- ASTM (American Society for testing and Materials), 'Metal Corrosion, Erosion and Wear', Annual Book of ASTM Standards (1987) 0.3.02, G1-72.
- M.I.H. Kittur and C.S. Mahajanshetti, *J. Oil Tech. Assoc. (India)* **16** (1984) 49.
- G. Schmitt, *Brit. Corros. J.* **19** (1984) 165.
- M.A. Quraishi, M.A.W. Khan, M. Ajmal, S. Muralidharan and S.V. Iyer, *J. Appl. Electrochem.* **26** (1996) 1253.
- M. Schorr and J. Yahalom, *Corros. Sci.* **12** (1972) 867.

18. R.T. Vashi and V.A. Champaneri, *Ind. J. Chem. Tech.* **4** (1997) 180.
19. 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.
20. I.N. Putilova, S.A. Balezin and U.P. Baranik, 'Metal Corrosion Inhibitors' (Pergamon Press, New York, NY: 1960), p. 31.
21. G.K. Gomma and M.H. Wahadan, *Ind. J. Chem. Tech.* **2** (1995) 107.
22. S. Brinic, Z. Grubac, R. Babic and M. Metikos-Hukovic, 'Study of the thiourea adsorption on iron in acid solution', Proceedings of 8th European Symposium on 'Corrosion Inhibition', Ann Univ, Ferrara, Italy **1** (1995), pp. 197–205.
23. M. Elachouri, M.S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert and E. Essassi, *Corrosion* **52** (1996) 103.
24. M.A. Quraishi, M.A.W. Khan, M. Ajmal, S. Muralidharan and S. Angappan, *Portg. Electrochim. Acta* **13** (1995) 63.
25. S.T. Hirozawa, Proceedings of the 8th European Symposium on 'Corrosion Inhibition', Ann. Univ. Ferrara, Italy, **1** (1995) p. 25.
26. N.C. Subramaniam and S. Mayanna, *Corros. Sci.* **25** (1985) 163.
27. P. Li, T.C. Tan and J.Y. Lee, *Corrosion* **53** (1997) 186.