Corrosion inhibition of mild steel in HCl solution by Tinidazole

Imran Reza, A. R. Saleemi, S. Naveed

University of Engg& Tech, Department of Chemical Engineering, Lahore, Pakistan, e-mail: imranreza@gmail.com, e-mail: darsaleemi@yahoo.com, e-mail: drsnaveed@uet.edu.pk

Tinidazole, a pharmaceutical compound has been investigated with reference to the inhibition of mild steel acidic corrosion in 1 molar HCl by means of weight loss and electrochemical measurements. The outcomes attained at 30°C revealed that the Tinidazole had obtained 90% inhibition efficiency at 400 ppm concentration. These results explain that the inhibition process occurs by means of adsorption. The inhibitor molecules adsorb on the surface of the metal, following Langmuir`s adsorption isotherm. Potentiodynamic polarization measurements established that Tinidazole is an inhibitor of a mixed type. An appropriate equivalent electric circuit for modeling and the analysis of impedance data to give a better explanation of the process of corrosion inhibition have been proposed.

Keywords: Acid corrosion, mild steel, Polarization, EIS, Tinidazole.

INTRODUCTION

Organic inhibitors that contain nitrogen, oxygen or sulphur have been reported as good inhibitors for mild steel in acidic medium[1, 2, 3]. Acidic solutions *i.e.* typically HCl are extensively used for various industrial purposes like boilers and eat exchangers descaling, acidic cleaning, pickling; acidizing of oil wells and so on[4]. For corrosion protection, the efficiency of organic compounds had been construed relating to molecular construction, size, mass and the heteroatoms presence[5]. For the explanation of inhibition mechanism of these compounds in acidic medium; adsorption on the metal surface is an important phenomenon[6]. In recent years, extensive research has been conducted for the development of drugs as corrosion inhibitors. Several reports are accessible in the literature concerning the influence of pharma drugs on the metallic corrosion[7 - 13].

Tinidazole is a second generation antibiotic drug that is characterized by strong activity on protozoa and anaerobic bacteria. It is extensively recognized all over Europe and the developing countries as the treatment for diversified amoebic and parasitic infections. The molecular mass of Tinidazole is 247.27 g mol^{-1} and its chemical structure is shown in Fig. 1. In accessible literature no data about the inhibitive action of Tinidazole of metallic corrosion is available. The present paper describes the role of Tinidazole for mild steel corrosion inhibition in the HCl solution using gravimetric, polarization and the EIS methods.
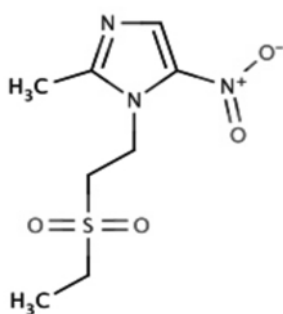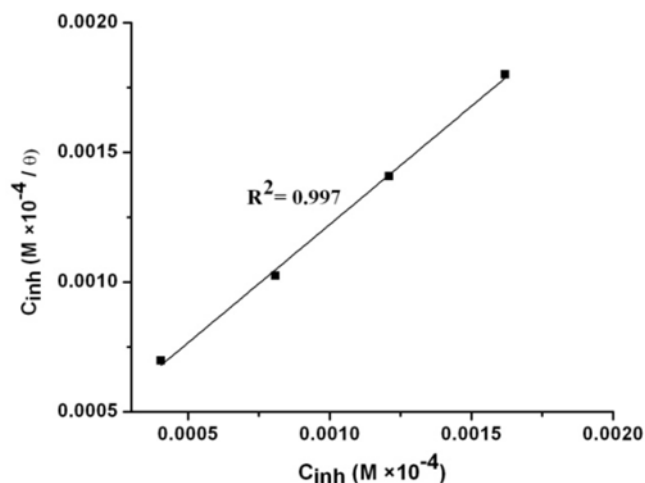

Figure 1. The Langmuir adsorption isotherm plot for the adsorption of the inhibitor on the mild steel surface in 1 M HCl. at 30°C

EXPERIMENTAL

For the weight loss experiments rectangular metallic coupons 5.0 cm × 2.0cm × 0.1cm were used. The composition (by weight) of the coupons is (C: 0.17%, Mn: 0.04%, Si: 0.10%, S: 0.026%, P: 0.032% and Fe: remaining). Before employing, the samples had been abraded by emery papers up to 800 grade and cleaned with double distilled water. Ethanol was used for the final cleansing of the samples. The corrosive solution of 1.0 M HCl (AR grade) was prepared in distilled water and used for all studies.

The same concentration of acid solution has been used for weight loss as well as the electrochemical experiments. Tinidazole, in pure form, was procured. The experimental studies were performed at room temperature i.e. 30±1°C. The immersion time for the gravimetric measurements was 3 hrs. The I.E (%) and (θ) were calculated from equations (1) and (2), respectively:

$$I.E\ (\%) = \frac{W_0 - W_i}{W_0} \times 100 \tag{1}$$

$$\theta = \frac{W_0 - W_i}{W_0} \tag{2}$$

Figure. The molecular structure of Tinidazole

where, W_0 and W_i represent the amount of weight loss before and after adding the inhibitor, respectively. I.E (%) denotes inhibition efficiency and θ is the surface coverage.

For the electrochemical studies three electrode cells were used. The area of each working sample in contact with the corrosive environment was 1.0 cm². The rest of the samples was isolated from the working environment by a cold mounting process, for which epoxy resin had been used. A glassy carbon rod was the counter electrode. The SCE electrode was used as a reference electrode. The working electrodes were prepared according to the standard procedure stated earlier. Gamry Potentiostat (Reference-600) with DC-105, EIS-300 and Echem Analyst 5.58 software was used to perform the experiments and the analysis of the data. All the measurements were made in a 200 ml working solution *i.e.* 1.0 M HCl. The (linear) polarization experiments were conducted at ±0.02 V around the open corrosion potential (OCP) and at the sweep rate of 0.125 mVs⁻¹. The I.E (%) was calculated from equation (3),

$$I.\,E\ (\%) = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \qquad (3)$$

R_p^i and R_p^0 are the measured values of polarization resistances, before and after adding the inhibitor, respectively.

The potentiodynamic polarization measurements were carried at ± 250mV vs. OCP. The sweep rate was 0.5mVs⁻¹. The Tafel method was adopted to acquire the values of (I_{corr}). The I.E (%) was estimated by the following expression, while, I_{corr}^0 and I_{corr}^i are corrosion current densities in the absence and presence of the inhibitor, respectively.

$$I.\,E\ (\%) = \frac{i_{corr}^0 - i_{corr}^i}{i_{corr}^0} \times 100 \qquad (4)$$

The impedance studies were performed as described, elsewhere[11]. Equation (5) was adopted for the calculations of I.E (%).

$$I.\,E\ (\%) = \frac{R_{ct}^i - R_{ct}^0}{R_{ct}^i} \times 100 \qquad (5)$$

R_{ct}^i and R_{ct}^o correspond to the values of charge transfer resistances in the absence and presence of inhibitor in the aggressive solution.

RESULTS AND DISCUSSION

Weight loss studies

The calculated parameters *i.e.* the values of corrosion rates (CR) and respective inhibition efficiencies (I.E %) by weight loss measurement are demonstrated in Table 1. From this table it is apparent that I.E (%) increase with the increment in the concentration of the inhibitor. 90 % inhibition efficiency was achieved at the 400 ppm inhibitor concentration. No considerable effect on the I.E % was observed by a further increase in Tinidazole concentration in the acid solution. This inhibitive performance is ascribed to the molecular adsorption of Tinidazole which takes place at the metallic surface. The adsorption may occur through π-electrons and also the non-bonding electron pairs[14]. Tinidazole contains p-orbitals and lone pairs

Table 1. The corrosion parameters for mild steel in 1M HCl solution with and without the inhibitor from the weight loss measurement at 30 °C for 3 hrs

Inhibitor Conc. / ppm	Weight Loss/ mg cm⁻²	Corrosion Rate/ mm year⁻¹	I.E/ %
0	13.36	49.75	
100	5.61	20.89	58
200	2.81	10.45	79
300	1.87	6.96	86
400	1.34	4.97	90
500	1.34	4.97	90

on heteroatoms, which play an important role and proposes ability of bonding of the inhibitor to the surface of metal. The inhibitive action may also be attributed to these properties.

Adsorption isotherm

To understand the adsorptive quality of an organic inhibitor, the study of adsorption isotherm is of pragmatic importance. Major information about the interface between the molecules of the inhibitor and the metallic surface may be obtained by the detailed study of adsorption isotherms The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundluich. These isotherm models were employed and the Langmuir's isotherm was found to be the best descriptive for the adsorption behavior according to the following equation:

$$\frac{\theta}{1 - \theta} = KC \qquad (6)$$

θ versus C/θ was plotted that yields a straight line (Fig. 2). The regression coefficient, R^2 of this line is 0.997. This suggests that the adsorption of the inhibitor used in this study conforms to the Langmuir`s isotherm. It also indicates that the interaction between the adsorbed molecules is insignificant.
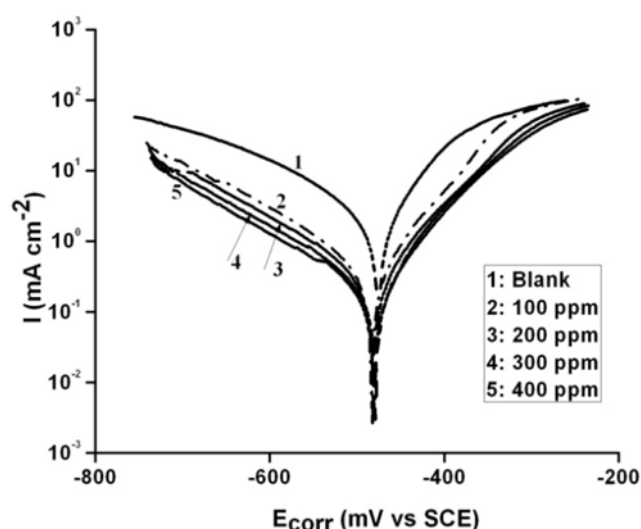

Figure 2. The potentiodynamic polarization behavior of mild steel in 1 M HCl with and without the addition of Tinidazole at30°C

Electrochemical studies

(Linear) polarization resistance

Changes in R_p of mild steel are shown in Table 2. The (R_p) values of mild steel increase from 15.6 Ω cm² in the

Table 2. The polarization parameters for the corrosion of mild steel in 1 M HCl with and without the inhibitor at 30°C

Inhibitor Conc. / ppm	Linear Polarization		Tafel Polarization				
	R_p / Ωcm^2	I.E / %	E_{corr} / mV vs.SCE	β_a / mV dec^{-1}	β_c / mV dec^{-1}	I_{corr} / $\mu A\ cm^2$	I.E / %
0	15.6		476	68.1	123.2	1570	
100	60.2	74.1	483	72.9	128.4	385	75.4
200	82.1	80.1	481	73.4	123.7	278	82.3
300	120.6	87	478	68.5	140.1	225	85.7
400	141.8	89	479	70.9	169.2	192	87.8

absence of Tinidazole to 141.8 Ω cm^2 of 400 ppm of its concentration. This behavior shows that with the increase of inhibitor concentration, the polarization resistance decreases resulting in the decrease of mild steel corrosion.

Potentiodynamic polarization studies

Fig. 3 shows the anodic and cathodic polarization curves for mild steel in 1.0 M HCl without and with different
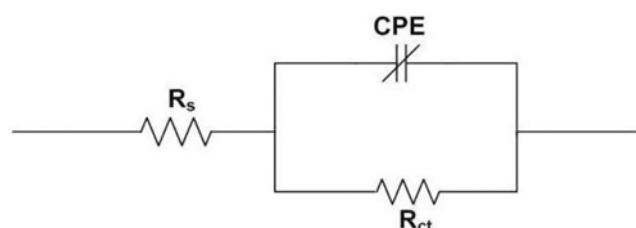
Figure 3. An equivalent circuit model for the impedance studies

concentrations of Tinidazole. These curves were extrapolated to calculate the current density (I_{corr}) and corrosion potential (E_{corr}). Different parameters evaluated from these studies are summarized in Table 2. It has been observed that variation in the cathodic Tafel slopes (ßc) is not appreciably large with the increase of Tinidazole concentration. This shows that cathodic reaction of hydrogen evolution was not affected by the addition of the inhibitor and no modifications occurred in this mechanism[15]. There was no significant change in E_{corr} without and with the addition of the inhibitor. According to Riggs[16], if E_{corr} displacement is greater that 85 mV relating to E, the type of the compound can be classified as either a cathodic inhibitor or an anodic inhibitor. If the change in E_{corr} is less than 85 mV, the corrosion inhibitor may be regarded as a mixed type. Our studies show that Tinidazole is a mixed type of an inhibitor. As in Table 2, the values of I_{corr} decrease from 1570 μA cm^{-2} to 192 μA cm^{-2} in the presence of 400 ppm Tinidazole, resulting in the efficiency of 87.8%.The values of the slope of cathodic curves (ßc) show little change in the presence of Tinidazole. These results suggest that there has been no change or modification in the mechanism of the reaction at the electrode surface[17].

Electrochemical impedance spectroscopy (EIS) studies

In Fig. 4, the Nyquist plots of impedance are presented. Because of the charge transfer of the process, at high frequency region a single semicircle has been observed. While increasing the inhibitor concentration, the values of charge transfer resistance enhanced. As in Fig. 3b, the perfect semicircles are not present. For the purpose of fitting and the analysis of the data evaluated by EIS, an equivalent circuit model has been proposed as in Fig. 4. In the pro-
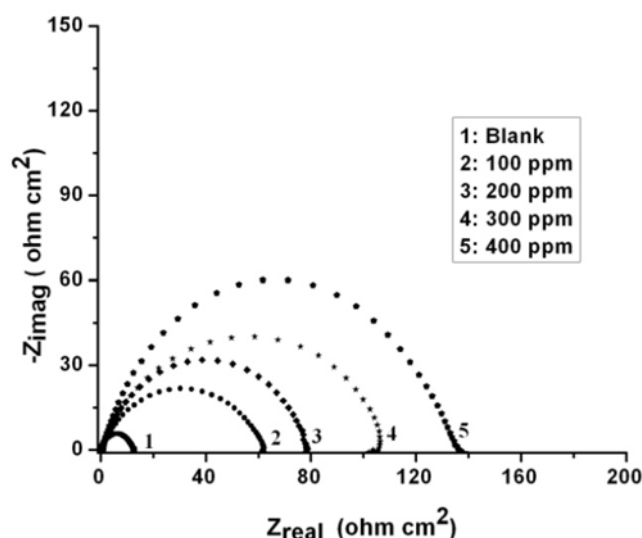
Figure 4. The Nyquist plot for mild steel behavior in 1 M HCl with and without the addition of the inhibitor at 30°C

posed circuit, R_{ct} is the charge transfer resistance, R_s is the solution resistance, and CPE is a constant phase element.

What follows is the impedance function of CPE:

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-1} \qquad (7)$$

Where, ω is the angular frequency ($\omega = 2\pi f_{max}$), Y is the CPE magnitude and the deviation parameter is "n" which describes the surface roughness. For n = 0, Z_{CPE} presents the resistance with R = Y^{-1}; n = 1 an ideal capacitor with C = Y; n = -1 an inductance with L = Y^{-1}. The behavior as an ideal capacitor is not practical in the real steel /acid interface systems. The reasons may be the surface roughness or uneven distribution of the current.[18, 19]; thus a constant phase element is introduced as an alternative of a capacitor to fit the impedance data with more accuracy. The double layer capacitance can be regarded as the idealized capacitance (C_{id}):

$$C_{id} = \frac{Y\omega^{n-1}}{\sin\left(n\frac{\pi}{2}\right)} \qquad (8)$$

The impedance data were fitted consistently with the equivalent circuit model. The parameters C_{dl}, R_{ct} and I.E (%) are summarized in Table 3. It has been noticed that the R_{ct} values increased with the increment of the inhibitor concentration. This indicates that the corrosion process was mainly controlled by the charge transfer process. The decrease in the C_{dl} values was induced by the steady displacement of water molecules. The phenomenon is actually originated by the molecular adsorption of the corrosion inhibitor on the surface of metal. This adsorptive phenomenon diminishes the intensity of dissolution reaction[20]. A protective layer forms on the mild steel surface due to the

Table 3. The EIS parameters for the corrosion of mild steel in 1 M HCl with and without the inhibitor at 30°C

Inhibitor Conc./ ppm	R_s/ $\Omega\ cm^2$	R_{ct} / $\Omega\ cm^2$	n	Y_0 / $10^{-6}; \Omega^{-1}\ cm^{-2}$	C_{td} / $\mu F\ cm^{-2}$	I.E / %
0	0.545	12.9	0.780	809	188	
100	0.622	62.2	0.782	427	123	79.2
200	0.648	78.4	0.788	338	106	83.5
300	0.702	105.9	0.790	319	106	87.8
400	0.714	136.6	0.795	247	88	90.5

adsorption of the inhibitor molecules at the metal/solution interface. This results in a decrease in the Cdl values with increasing the concentration of the inhibitor[21]. The depth of this protective double layer (d_{org}) is associated with C_{dl} according to the Helmholtz model:

$$C_{dl} = \frac{\varepsilon \varepsilon_0}{d_{org}} \tag{9}$$

Where ε is the dielectric constant of the protective double layer and ε_0 is the permittivity of free space (8.854×10^{-14} F cm^{-1}). In addition, an inductive loop has been observed for both the inhibited and uninhibited solutions. The inductive loop at low frequency may be present due to the process of relaxation which is caused by the adsorption of species like $(Cl^-)_{ads}$ and $(H^+)_{ads}$ on the electrode surface. This can be ascribed to the re-dissolution of protective layer[23].

CONCLUSIONS

All results obtained proved that Tinidazole has good properties for the corrosion inhibition of mild steel in the studied medium *i.e.* 1 molar HCl solution. The weight loss results establish that the efficiency increased with an increase in Tinidazole concentration. 90.5% efficiency was achieved at the 400 ppm concentration of Tinidazole. The potentiodynamic polarization experiments demonstrate the type of the inhibitor and showed that Tinidazole is of a mixed type. Impedance measurements also designate that the charge transfer resistance was increased by the inhibitor. The inhibitive performance of Tinidazole depends on the adsorption of its molecules on the metallic surface. The results determined by all the experimental techniques are in convincingly good agreement.

The adsorption model obeys the Langmuir isotherm.

LITERATURE CITED

1. Abdel-Aal, M.S. & Morad, M.S. (2001). Inhibiting effects of some quinolines and organic phosphonium compounds on corrosion of mild steel in 3M HCl solution and their adsorption characteristics Br. Corros. J. 36,253-260.DOI:10.1179/000705901101501703.

2. Abdel-Gabar, A.M., Abd-El-Nabey, B.A.,Sidahmed, I.M., El-Zayady, A.M. & Saadawy, M.(2006).Inhibitive action of some plant extracts on the corrosion of steel in acidic media. Corros.Sci. 48, 2765-2779.DOI:10.1016/j.corsci.2005.09.017.

3. Bommersbach, P., Alemany-Dumont, C., Millet, J.P. & Normand, B.(2005). Formation and behaviour study of an environment-friendly corrosion inhibitor by electrochemical methods. Electrochim.Acta 51, 1076-1084.DOI:10.1016/j.electacta.2005.06.001.

4. Schmitt, G. (1984).Application of inhibitors for acid media. Br. Corros. J. 19,165-176.

5. Muralidharan, S., Quraishi, M.A. & Iyer, S.V.K. (1995). The effect of molecular structure on hydrogen permeation and the corrosion inhibition of mild steel in acidic solutions Corros. Sci. 37, 1739-1750.DOI:10.1016/0010-938X(95)00068-U.

6. Rudresh, H.B. & Mayanna. (1977). Adsorption of n-Decylamine on Zinc from Acidic Chloride Solution. J. Electrochem. Soc. 124, 340-342.DOI:10.1149/1.2133301.

7. Abdallah, M.(2002). Rhodanineazosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution.Corros. Sci. 44, 717-728. DOI:10.1016/S0010-938X(01)00100-7.

8. Abdallah, M. (2004).Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution.Corros. Sci. 46, 1981-996.DOI:10.1016/j.corsci.2003.09.031.

9. Prabhu, R.A., Shanbhag, A.V., &V enkatesha, T.V. (2007). Influence of tramadol [2-[(dimethylamino)methyl]-1-(3-methoxyphenyl) cyclohexanol hydrate] on corrosion inhibition of mild steel in acidic media. J. Appl. Electrochem. 37, 491-497.DOI:10.1007/s10800-006-9280-2.

10. Morad, M.S. (2008). Inhibition of iron corrosion in acid solutions by Cefatrexyl: Behaviour near and at the corrosion potential. Corros.Sci. 50, 436-448. DOI:10.1016/j.corsci.2007.08.018.

11. Shukla, S.K., Singh, A.K., Ahamad, I. & Quraishi, M.A. (2009). Streptomycin: A commercially available drug as corrosion inhibitor for mild steel in hydrochloric acid solution Mater.Lett. 63, 819-822.DOI:10.1016/j.matlet.2009.01.020.

12. Obot, I.B. Obi-Egbedi, N.O. & Umoren, S.A. (2009). Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl.Corros. Sci. 51, 1868-1875. DOI:10.1016/j.corsci.2009.05.017.

13. Singh, A.K. &Quraishi, M.A.(2010). Effect of Cefazolin on the corrosion of mild steel in HCl solution.Corros. Sci. 52, 152-160. DOI:10.1016/j.corsci.2009.08.050.

14. Bentiss, F. Traisnel, M. & Lagrenee, M. (2000). Inhibition of acidic corrosion of mild steel by 3,5-diphenyl-4H-1,2,4-triazole. Appl. Surf. Sci. 161, 194-202.DOI:10.1016/S0169-4332(00)00287-7.

15. Li, W., He, Q., Zhang, S., Pei, C. & Hou, B. (2008). Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium. J. Appl. Electrochem. 38, 289-295. DOI:10.1007/s10800-007-9437-7.

16. O.L. Riggs Jr., Corrosion Inhibition, second ed., C.C. Nathan, Houston, TX, 1973.

17. Bentiss, F.,Gassama, F., Barbry, D.,Gengembre, L.,Vezin, H.,Lagrenée, M. & Traisnel, M.(2006). Enhanced corrosion resistance of mild steel in molar hydrochloric acid solution by 1,4-bis(2-pyridyl)-5H-pyridazino[4,5-b]indole: Electrochemical, theoretical and XPS studies. Appl. Surf. Sci. 252, 2684-2691.DOI:10.1016/j.apsusc.2005.03.231.

18. Macdonald, J.R. (1987).Impedance spectroscopy and its use in analyzing the steady-state AC response of solid and liquid electrolytes. J. Electroanal. Chem. 223,25-0.DOI:10.1016/0022-0728(87)85249-X.

19. Pang, J., Briceno, A. & Chander, S. (1990).A Study of Pyrite/Solution Interface by Impedance Spectroscopy. J. Electrochem. Soc. 137, 3447-3455.DOI:10.1149/1.2086249.

20. Lagrenee, M., Mernari, B., Bouanis, M., Traisnel, M. & Bentiss, F. (2002). Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on

mild steel corrosion in acidic media.Corros. Sci. 44, 573-588.DOI:10.1016/S0010-938X(01)00075-0.

21. Srhiri, A., Etman, M. & Dabosi, F. (1992).Thiol compounds as corrosion inhibitors of carbon steel (XC 38) in sodium chloride medium. WerkstKorros 43, 406-414. DOI:10.1002/maco.19920430806.

22. Popova, A., Sokolova, E., Raicheva, S. & Christov, M. (2003). AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives.Corros. Sci. 45, 33-58.DOI:10.1016/S0010-938X(02)00072-0.

23. Hassan, H.H., Abdelghani, E. & Amin, M.A. (2007). Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part I. Polarization and EIS studies.Electrochim.Acta52, 6359-6366.DOI:10.1016/ j.electacta.2007.04.046.