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Inhibitive Action of *p*-Toluidine on Corrosion of Zinc in H_2SO_4 Medium

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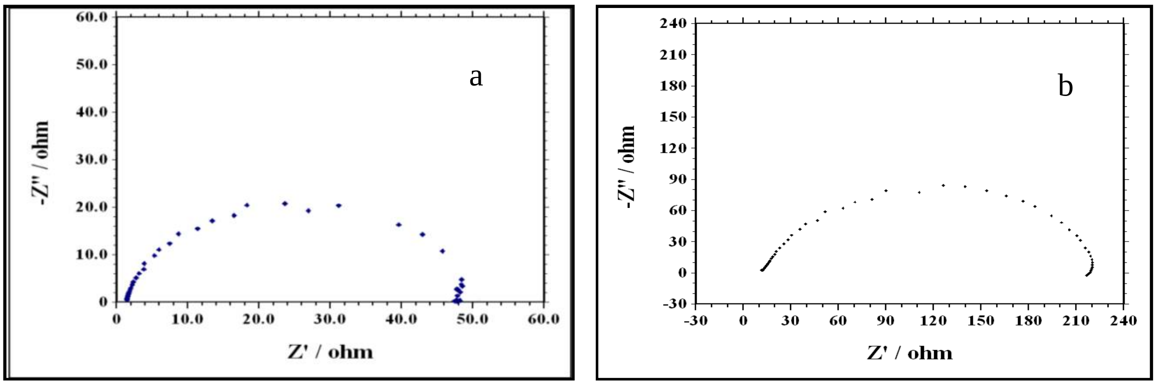
ABSTRACT

In the present study, the inhibition of the corrosion of zinc in H_2SO_4 solution by p-toluidine has been studied by using weight loss, Potentiodynamic Polarization and Electrochemical Impedance Spectroscopic (EIS) methods. Corrosion rate increases with the increase in acid concentration and temperature. As inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (I.E.) increases. At constant inhibitor concentration corrosion rate and I.E. increases with increase in acid concentration. p-toluidine showed maximum I.E. of 94.87 % at 60 mM in 0.5 M H_2SO_4 acid at 301 K. The value of free energy of adsorption (ΔG^0_{ads}), heat of adsorption (Q_{ads}), energy of activation,(E_a), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated. Plot of log [$\theta/(1-\theta)$] vs. log C shows straight line with almost unit slope, which suggest that the inhibitor cover both anodic and cathodic regions through general adsorption following Langmuir isotherm. Polarization curve indicates that inhibitor act as mixed type. The results obtained showed that the p-toluidine could serve as an effective inhibitor for corrosion of zinc in H_2SO_4 acid.

Graphical Abstract



Nyquist plots for corrosion of zinc in 0.1 M H_2SO_4 (a) in absence and (b) in presence of inhibitor.

Keywords: Zinc, H_2SO_4, Corrosion, *p*-Toluidine, Polarization and EIS.

INTRODUCTION

Corrosion is a phenomenon that affects all metals; it results from physicochemical interaction between materials and its environment, entailing changes in their properties, led to significant economic losses.Zinc is extensively used for coating or galvanizing ferrous metal products due to its better resistance to atmospheric corrosion than carbon steel. Sulphuric acid (H_2SO_4) is a strong acid and is used as a cleaner for rust, algae and scale from condensers and cooling tower [1]. A.S. Fouda *et al.*, [2] studied thiophine derivatives as corrosion inhibitors for CS in 0.5 M H_2SO_4. Desai and Malik [3] studied inhibition property of Caesalpinia Crista on corrosion of mild steel in H_2SO_4.The influence of organic compounds on the corrosion of zinc in acidic solutions has been investigated by several authors [4-12]. Many researchers [13-17] have studied toluidine isomers as corrosion inhibitors in different acid media. The aim of the present study is to investigate the corrosion inhibition effect of *p*-toluidine for zinc in various concentration of H_2SO_4 medium by weight loss, effect of temperature, polarization and EIS techniques.

MATERIALS AND METHODS

Preparation of sample and solution: The zinc specimens with a chemical composition of 99.39 % Zn, 0.49 % Mn and 0.12 % Co were used in the present study. The metal sheet, test specimens of size 5.0 x 2.5 x 0.2 cm having an effective area of 0.3013 dm^2 was used. The specimens were cleaned by washing with distilled water, degreased by acetone, washed once more with doubled distilled water and finally dried and weighted by using electronic balance. Sulphuric acid was used as corrosive solution having concentration of 0.1, 0.3 and 0.5 M prepared by diluting analytical grade of H_2SO_4 purchased from Merck using double distilled water.

Weight loss measurements: For weight-loss measurement, the zinc coupons were each suspended and completely immersed in 230 mL of various concentrations like 0.1, 0.3 and 0.5 M H_2SO_4 solution without and with different concentrations of *p*-toluidine at 301± 1 K for 24 h immersion period. After the test, the specimen was cleaned by using 10 % Chromic acid solution having 0.2 % $BaCO_3$ [18]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier and reweight. From the weight loss data, corrosion rate (CR) was calculated.

Temperature effect: To study the effect of temperature on corrosion of zinc in 0.1 M H_2SO_4, the specimens were immersed in 230 mL of the corrosive solution and weight loss was determined at solution temperature of 313, 323 and 333 K for an immersion period of 3h in absence and presence of *p*-toluidine at 30, 40, 50 and 60 mM concentration. Attention is paid to compensate the evaporation loss of corrosive media. From the data, corrosion rate (C.R), inhibition efficiency (I.E.), activation energy (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG^0_{ads}), enthalpy of adsorption (ΔHa) and entropy of adsorption (ΔSa) were calculated.

Potentiodynamic polarization measurements: For polarization study, metal specimens having as area of 1 cm^2 were immersed to 230 mL 0.1 M H_2SO_4 in absence and presence of *p*-toluidine in the test cell (CH instruments, Inc., USA) includes the metal specimens as a working electrode, Ag/AgCl electrode as a reference electrode as well as platinum electrode as an auxiliary electrode. Before each electrochemical measurement, the working electrode was allowed to stand for 65 min. in test allowed to establish a steady-state open circuit potential (OCP). Polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (icorr) and the corrosion potential (Ecorr) [19]. Cathodic Tafel slope (βc) and anodic Tafel slope (βa) were calculated from the software installed in the instrument.

Electrochemical Impedance Spectroscopy (EIS) measurements: EIS measurements were made (CH instruments, Inc., USA) at corrosion potentials over a frequency range of 1 KHz to 100 KHz by a sine wave with potential perturbation amplitude of 5 mV. The real Z' and imaginary -Z''parts were measured at various frequencies. From the plot of Z' Vs. -Z'', the charge transfer resistance (Rct), and double layer capacitance (Cdl) were calculated. Impedance measurements were carried out both in the absence and presence of inhibitor.

RESULTS AND DISCUSSION

Weight loss experiments: The weight loss experiment was carried out in 0.1, 0.3 and 0.5 M H_2SO_4 solution containing 30, 40, 50 and 60 mM concentration of *p*-toluidine at 301±1 K for a exposure period of 24 h was investigated. Corrosion rate (C.R.) was calculated using following equation:

$$\text{C.R. (mg/dm}^{2}\text{d)} = \text{Weight loss (gm.) x 1000 / Area in dm}^{2}\text{ x day} \qquad ..(1)$$

Inhibition efficiency (I.E.) was calculated by using following equation:

$$\text{I.E. (\%)} = \left\{\frac{(W_u - W_i)}{W_u}\right\} \times 100 \qquad ..(2)$$

Where: Wu = Weight loss in absence of inhibitor, Wi = Weight loss in presence of inhibitor.

The degree of surface coverage (θ) of the zinc specimen for different concentration of H_2SO_4 solution has been evaluated by weight loss experiments using the following equation:

$$\theta = \frac{(W_u - W_i)}{W_i} \qquad ..(3)$$

Effect of acid concentration: Results showed in Table-1 indicates that as the acid concentration increases corrosion rate increases. Corrosion rate was 1035.50, 2880.84 and 6179.88 $mg/dm^{2}.d$ corresponding to 0.1, 0.3 and 0.5 M H_2SO_4 concentrations respectively for an immersion period of 24 h at 301± 1 K. At constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 60 mM inhibitor concentration, the I.E. of *p*-toluidine was 91.66, 93.53 and 94.87 % with respect to 0.1, 0.3 and 0.5 M sulphuric acid concentration respectively (Table 1).

Effect of inhibitor concentration: At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while I.E. increases. e.g. in case of *p*-toluidine in 0.5 M H_2SO_4 the I.E. was found to be 73.03, 77.91, 91.37 and 94.87 % correspond to 30, 40, 50 and 60 mM inhibitor concentration respectively (Table 1, Figure 1).

Table 1. Effect of H_2SO_4 concentration on corrosion rate (CR) and I.E. of zinc having different concentrations of *p*-toluidine for an immersion period of 24 h at 301 ± 1 K.

Inhibitor	Inhibitor concentration (mM)	Acid Concentration					
		0. 1 M		0. 3 M		0. 5 M	
		CR (mg/ dm^{2}·d)	I.E. (%)	CR (mg/ dm^{2}·d)	I.E. (%)	CR (mg/ dm^{2}·d)	I.E. (%)
Blank	-	1035.50	-	2880.84	-	6179.88	-
p - Toluidine	30	325.45	68.57	869.43	69.82	1666.71	73.03
	40	279.48	73.01	660.28	77.08	1365.13	77.91
	50	109.03	89.47	284.33	90.13	533.32	91.37
	60	086.36	91.66	186.93	93.53	317.02	94.87

Temperature effect: To investigate the influence of temperature on corrosion of zinc, the weight loss experiments were also carried out at 313, 323 and 333 K in 0.1 M H_2SO_4 in absence and presence of 30, 40, 50and 60 mM inhibitor concentration for an immersion period of 3h. As the temperature

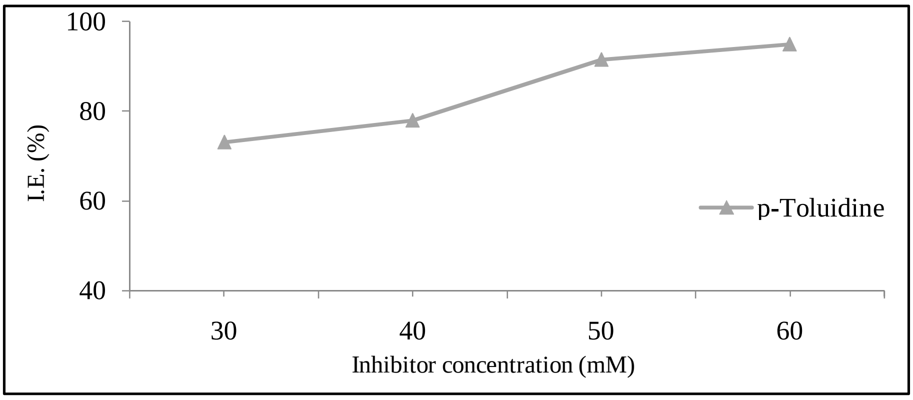


Figure 1. Effect of inhibitor concentration on inhibition efficiency (I.E.) of p-Toluidine for zinc in 0.5 M H_2SO_4 at 301 K for 24 h immersion period.

increases the corrosion rate was increases while percentage of I.E. decreases. Corrosion rate was increase as 10594.08, 12399.60 and 14709.52 mg/dm^{2}d corresponding to 313, 323 and 333 K respectively in 0.1 M H_2SO_4 (Table 2). Increase in corrosion rate with temperature may be due to the desorption of the adsorbed molecules inhibitor and thus exposing the fresh metal surface to further attack [20], which results in intensification of the kinetic of electrochemical reaction [21]. The addition of *p*-toluidine in corrosive media indicates that as the temperature increases I.E. decreases, e.g. in 0.1 M H_2SO_4 at 60 mM inhibitor concentration, the I.E. for *p*-toluidine was 74.43, 52.67 and 31.58 % at 313, 323 and 333 K respectively.

The value of energy of activation (E_a) has been calculated with the help of Arrhenius equation [22].

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad ..(4)$$

Where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

Table 2. Temperature effect on corrosion rate activation energy and heat of adsorption for zincin 0.1 M H_2SO_4 in absence and presence of *p*-toluidine for an immersion period of 3h.

Inhibitor concen-tration (mM)	Temperature						Mean (E_a) From Equation (4) (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	
	313 K		323 K		333 K			313-323 K	323-333 K
	CR mg/dm^{2}d	I. E. (%)	CR mg/dm^{2}d	I. E. (%)	CR mg/dm^{2}d	I. E. (%)			
Blank	10594.08	-	12399.60	-	14709.52	-	14.25	-	-
30	4858.88	54.13	9689.12	21.85	12107.52	17.68	39.77	-121.10	- 23.47
40	4115.44	61.15	7460.96	39.82	11443.68	22.20	44.39	- 72.86	- 75.23
50	3398.56	67.92	6664.40	46.25	11178.16	24.00	51.67	- 75.68	- 89.65
60	2708.24	74.43	5867.84	52.67	10063.04	31.58	56.99	- 80.83	- 77.57

Energy of activation (E_a): The mean "E_a" value calculated from equation (4) for zinc in 0.1 M H_2SO_4 was 14.25 kJ mol^{-1}. A comparison of the values of the E_a for the corrosion process in inhibited (in the range 39.77 to 56.99 kJmol^{-1}) which indicates that the "E_a" values were higher in inhibited than in uninhibited acid (Table 2). The higher values of mean E_a, indicates physical adsorption of the inhibitor on metal surface [23]. The value of Ea calculated from the slop of Arrhenius plot (Figure 2) and using equation (4) were almost similar.

Heat of adsorption (Q_{ads}): The values of heat of adsorption (Q_{ads}) were calculated by using the following equation [24]:

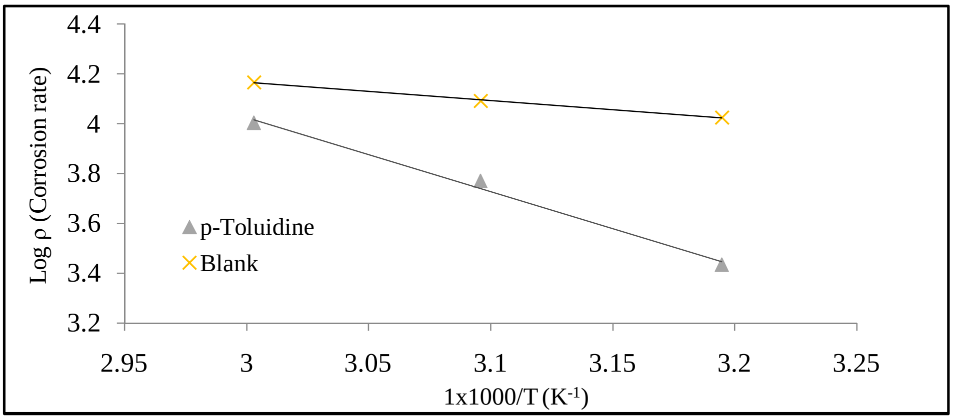


Figure 2. Arrhenius plots for corrosion of zinc in 0.1 M sulphuric acid in absence and presence of 60 mM inhibitor concentration.

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left[\frac{T_1T_2}{T_2-T_1}\right] \quad .. (5)$$

Where, θ_1 and θ_2 are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. From Table- 2 it was evident in all cases Q_{ads} values were negative and ranging from-23.47 to -121.10 kJ mol^{-1}. As the temperature increases values of Q_{ads} decreases (become more negative). The negative values of Q_{ads} shows that the adsorption process and hence the I.E. decreases with rise in temperature supporting the physisorption mechanism [25].

Adsorption isotherm: The applicability of Langmuir adsorption isotherm to the adsorption of *p*-toluidine on zinc coupons suggests strong adsorption of the inhibitor on the zinc surface and the existence of monolayer of the adsorbed inhibitor. This clearly shows that there are interactions between the active sites on the zinc surface and inhibitor species leading to the formation of spread films on the zinc surface and which consequently inhibited the corrosion process. Similar observations have been reported [26, 27]. A plot of inhibitor concentration log [θ / (1 - θ)] vs. log C for *p*-toluidine in 0.1 M H_2SO_4 was presented in figure 3 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm [28].

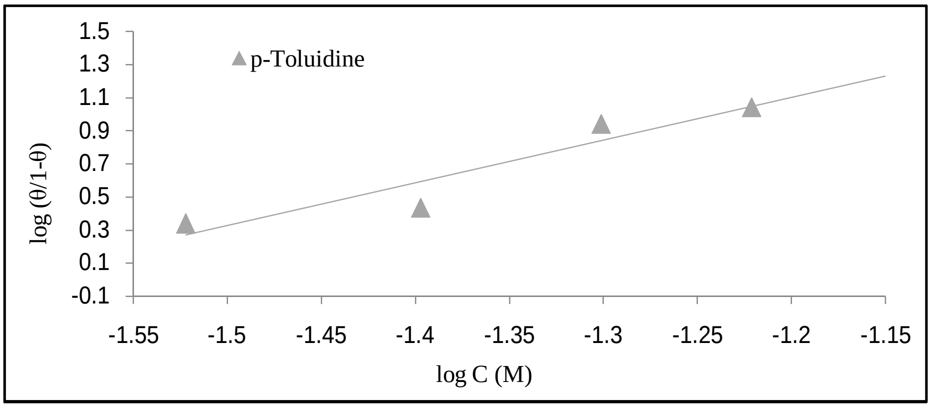


Figure 3. Plot of log [θ/(1 - θ)] versus log C for *p*-toluidine in 0.1 M H_2SO_4 at 301 K.

Free energy of adsorption (ΔG°$_a$): The values of the free energy of adsorption (ΔG_a) were calculated with the help of the following equation [29].

$$\log C = \log [(\theta / 1 - \theta)] - \log B \qquad .(6)$$

Where, $\log B = -1.74 - (\Delta G_a / 2.303\ RT)$, C is the inhibitor concentration and R is the gas constant. The mean value of ΔG^o_{ads} were found negative and ranging from -17.77 to -18.63 kJ mol^{-1}. The negative value of the standard free energy of adsorption indicate a spontaneous adsorption of this inhibitor on zinc. This means that the inhibitive action of this substance result from the physical adsorption of these molecules on the surface of zinc [8, 30]. This is concluded on the fact that the values of ΔG^o_{ads} -20 kJ mol^{-1} are consistent with physisorption, while those around -40 kJ mol^{-1} or higher are associated with chemisorptions [31]. This is also supported by the fact that the I.E. of the investigated inhibitor decreases at higher temperature.

Enthalpy of adsorption ($\Delta H°_{ads}$): ΔH^o_a was calculated using the equations (7)

$$\Delta H^o_a = E_a - RT \qquad .. (7)$$

Results indicates that values of ΔH^o_a were positive and increase in presence of inhibitor indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the zinc corrosion reaction. The enthalpy change ΔH^o_a was positive and ranging from 17.22 to 62.39 kJ mol^{-1} indicating the endothermic nature of the reaction suggests that higher temperature favours the corrosion process [32].

Entropy of adsorption ($\Delta S°_{ads}$): ΔS^o_a was calculated using the equations (8).

$$\Delta S^o_a = \Delta H^o_a - \Delta G^o_a / T \qquad .. (8)$$

The entropy ($\Delta S°_{ads}$) values were positive as 0.11 to 0.27 kJ mol^{-1} K^{-1} confirming that the corrosion process is entropically favourable [33].

Kinetic parameters: Rate constant (k) and Half-life ($t_{1/2}$): As concentration of inhibitor increases rate constant k decreases whereas the half-life increases (Table 3). The results are in good agreement with the result obtain by Muthukumar and Chandrasekaran [34]. Corrosion rate constant 'K' increases with increases in concentration of acid (Table 3). The values of half-life ($t_{1/2}$) were calculated by using the following equation [35]

$$t_{1/2} = 0.693 / k \qquad ..(9)$$

Where,'t' is time in hours and 'k' is rate constant.

Table 3. Kinetic data for the corrosion of zinc in various concentration of H_2SO_4containing*p*- Toluidine as an inhibitor

Inhibitor	Inhibitor concentration (mM)	Acid Concentration					
		0.1 M		0.3 M		0.5 M	
		Rate constant k x 10^{-3} day^{-1}	Half-life $t_{1/2}$ day^{-1}	Rate constant k x 10^{-3} day^{-1}	Half-life $t_{1/2}$ day^{-1}	Rate constant k x 10^{-3} day^{-1}	Half-life $t_{1/2}$ day^{-1}
Blank	-	15.9	43.45	45.07	15.37	99.97	6.93
p - Toluidine	30	4.90	139.32	13.35	51.91	26.23	26.42
	40	4.30	159.82	10.16	68.21	21.10	32.84
	50	1.60	428.31	4.36	158.94	8.20	84.41
	60	1.30	522.62	2.85	242.81	4.88	142.01

Potentiodynamic polarization study: Potentiodynamic polarization curve of zinc in 0.1 M H_2SO_4 in absence and presence of 60 mM *p*-toluidine were shown in figure 4 and figure 5. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) anodic Tafel slope (βa), cathodic Tafel slope (βc) and percentage I.E. were given in table 4. The curves show polarization of both, the cathodes as well as anodes. I.E. calculated from corrosion current obtained by the extrapolation of the cathodic and anodic Tafel lines were given in table 4. In almost all the cases, the I.E. from Tafel plots agree well (within ± 3 %) with the values obtained from weight loss data.

Table 4. Potentiodynamic polarization data and Inhibition efficiency (I.E.) of *p*-toluidine as an inhibitor for zinc in 0.1 M H_2SO_4

System	E_{corr} (V)	I_{corr} (μA /cm^2)	Tafel slope (V / decade)			IE (%) Calculated from	
			Anodic (+βa)	Cathodic (-βc)	β (V)	Weight loss method	polarization method
Blank	-1.094	2.2320	0.4133	0.2191	0.0622	-	-
p - Toluidine	-1.040	0.2554	0.1202	0.1820	0.0314	91.66	88.55

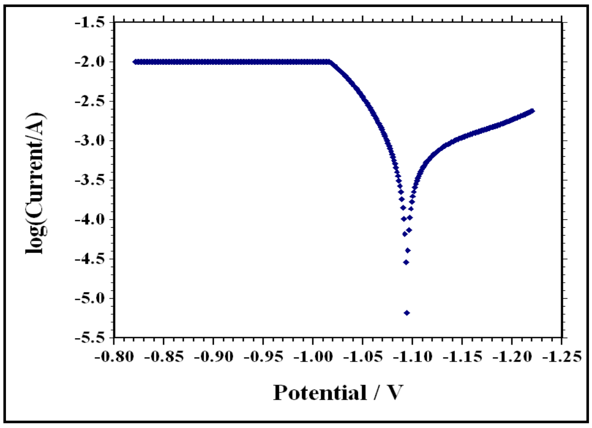


Figure 4. Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 in absence of inhibitor.

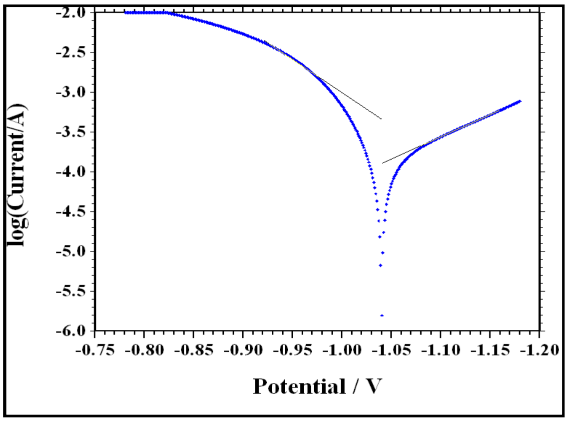


Figure 5. Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM *p*-Toluidine.

From table 4, it was observed that the addition of *p*-toluidine in acid solution indicates the significant decrease in corrosion current density (i_{corr}) and decrease in corrosion rate with respect to blank. There is significant change in the anodic and cathodic slopes after the addition of the inhibitors. In general, an inhibitor is anodic or a cathodic if the variation of E_{corr} against the blank is higher or above than 85 mV [36, 37]. In this study, the displacement of the E_{corr} was about 54 mV (Table 5) which suggest that *p*-toluidine should be considered as mixed type of inhibitor.

Inhibition efficiency (I.E.) from polarization study was calculated using following equation [38].

$$\text{I.E. (\%)} = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \text{ X } 100 \qquad ..(10)$$

Where $i_{corr(uninh)}$ is corrosion current density for uninhibited acid and $i_{corr(inh)}$ corrosion current density for inhibited acid.

Electrochemical impedance spectroscopy (EIS) measurements: EIS technique was studied to investigate the growth of the film formed on metal surface by inhibitor. Corrosion of zinc in 0.1 M H_2SO_4 in presence of *p*-toluidine was investigated by EIS measurement at room temperature. Nyquist plots for zinc obtain in absence and presence of *p*-Toluidine was shown in (Figure 6 and Figure 7) and results are shown in table 5.

The diameter of capacitive loop in the presence of inhibitor is bigger than that in the absence of inhibitor. The high frequency capacitive loop is related to the charge transfer resistance (R_{ct}). To calculate the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum was found as presented in the following equation [39];

$$C_{dl} = \frac{1}{2\pi F_{max} R_{ct}} \quad ...(11)$$

Where' f' is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [40].

Table 5. EIS parameters for corrosion of zinc in 0.1 M H_2SO_4 containing p-Toluidine

System	R_{ct} (Ω cm^2)	C_{dl} (μF / cm^2)	I.E. (%) Calculated from	
			EIS method	Weight loss method
Blank	49.5	151.84	-	-
p - Toluidine	210.0	8.92	94.12	91.66

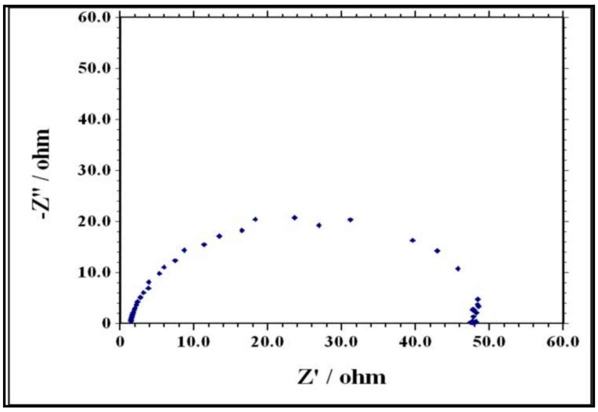


Figure 6. Nyquist plot for corrosion of zinc in 0.1 M H_2SO_4 in absence of inhibitor.

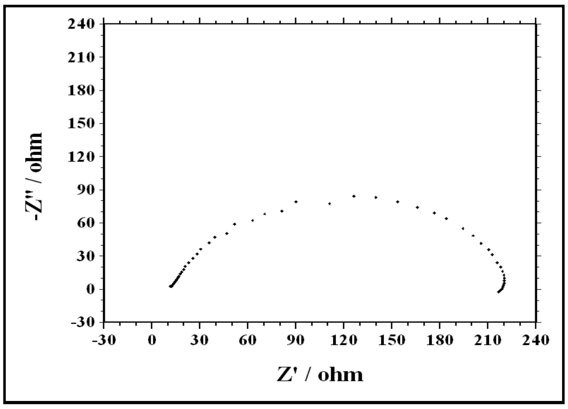


Figure 7. Nyquist plot for corrosion of zinc in 0.1M H_2SO_4 in presence of 60 mM *p*-Toluidine.

Inhibition efficiency (I.E.) from EIS method was calculated using following equation:

$$I.E.(\%) = \frac{Cdl(uninhi.) - Cdl(inhi.)}{Cdl\ (uninhi.)} \ x\ 100 \quad ..(12)$$

Where $C_{dl(uninhi)}$ is double layer capacitance for uninhibited acid and $C_{dl(inhi)}$ is double layer capacitance for inhibited acid.The addition of inhibitor increase R_{ct} value from 49.5 to 210.0 Ω cm^2, at the same time it decreases the C_{dl} values from 151.84 to 8.92 µF/cm^2 which is due to the adsorption of inhibitor on the metal surface (Table 5). The results suggest that the inhibitor acts by the formation of a physical protective layer on the surface that retards the charge transfer process and therefore inhibit the corrosion reaction, leading to increase in R_{ct} values. Moreover, the adsorbed inhibitor species decrease the electrical capacity of electrical double layer values at the electrode/solution interface and therefore decrease the value of C_{dl} [41]. It was observed that from that the impedance diagram was almost semicircle in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion [42]. The semicircle nature of the plots indicates that the corrosion of zinc is mainly controlled by charge transfer process.

Mechanism of corrosion of zinc: Corrosive attack of H_2SO_4 on zinc which may be mainly due to the formation of HSO_4^- during the ionization of acid. Sulphuric acid acts as strong acid. The probable chemical reaction taking place in sulphuric acid is as under. It undergoes hydrolysis in aqueous solution.

$$2H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + 2HSO_4^- \qquad ..(13)$$

Generally, zinc dissolves in H_2SO_4 solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad \text{(anodic reaction)} \qquad ..(14)$$

Reduction reaction is indicated by a decrease in valence or the consumption of electrons.

$$2H^+ + 2e^- \rightarrow 2H \text{ (ads)} \qquad \text{(cathodic reaction)} \qquad ..(15)$$

H_2 gas is liberated by any of the two following reactions:

$$H + H = H_2 \uparrow \qquad ..(16)$$

$$\text{Or} \quad H + H^+ + e- = H_2 \uparrow \qquad ..(17)$$

$$\text{Or} \quad H + H_3O^+ + e- = H_2 \uparrow + H_2O \qquad ..(18)$$

Mechanism of inhibition of corrosion by *p*-toluidine: Methyl group has + R (Resonance) effect and + I (Inductive) effect which increases the basicity of a -NH_2 group. The pka value of *p*-toluidine is 5.19 which increases the basicity of *p*-toluidine and shows higher I.E. Substitution of -CH_3 group suggest that resonance is capable of supplying electron density by resonance and inductive effect is expected to diminish the +ve charge assumed by *p*-toluidine.

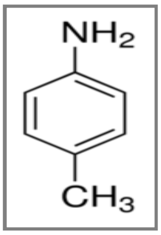


Figure 8. Structure of *p*-toluidine.

CONCLUSION

From the present study following conclusions can be drawn:

1. As acid concentration increases corrosion rate and I.E. increases.
2. At constant acid concentration, as inhibitor concentration increases corrosion rate decreases while I.E. increases.
3. As temperature increase corrosion rate increases while I.E. decreases.
4. *p*-toluidine showed maximum I.E. of 94.87 % at an optimum concentration of 60 mM in 0.5 M H_2SO_4.
5. The values of E_a obtained in the presence of inhibitors were higher compared to the blank acid solution which indicates that inhibitor was more effective at lower temperature.
6. The values of ΔG^o_{ads} were negative, which reveals the spontaneous adsorption of inhibitor onto metal surface.
7. The adsorption of *p*-toluidine on zinc surface obeyed Langmuir adsorption isotherm.
8. Polarization curves shows that the *p*-toluidine act as mixed type of inhibitor.

9. The results obtained from weight loss, polarization and EIS studies were in good agreement with each other.

REFERENCES

[1]. N. I. Sax, R. J. Sr. (eds.) Lewis, Hawley's Condensed Chemical Dictionary, 11th edition: New York. Van Nostrand Reinhold Co, **1987**.

[2]. A. S. Fouda, S. Abd El-Maksoud, S. A. Gomaa, A.Elsalakawy, Thiophene Derivatives as Corrosion Inhibitors for CS in 0.5 M H_2SO_4 Solutions, *J. Applicable Chem*., **2017**, 6(1), 160-175.

[3]. N. S. Desai, G.M. Malik,Inhibition Study of Caesalpinia Crista on Corrosion of Mild Steel in Sulphuric acid, *J. Applicable Chem.*, **2016**, 5(5), 1226-1235.

[4]. S. A. Zele, K. K. Patel, R. T. Vashi, Ethanolamines as corrosion inhibitors for zinc in sulphuric acid, *J. Applicable Chem*., **2017**, 6(3), 350-362.

[5]. A. Khulood, S. Saleh and Khalil, Corrosion inhibition study of zinc in 0.1 M HNO_3 by di phenylcarbazide and caffeine, *Physical Chem.; An Indian J.,* **2015**, 10(1), 32-40.

[6]. Lin Wang, Jian-XinPu and Hui-Chun Luo, Corrosion inhibition of zinc in phosphoric acid solution by 2-mercaptobenzimidazole, *Corros. Sci.,* **2003**, 45(4), 677-683.

[7]. A. S. Fouda, M. Abdallah, S. T. Atwa, M. M. Salem, Tetrahydrocarbazole derivatives ascorrosion inhibitors for zinc in HCl solution, *Modern Appl. Sci.,* **2010**, 4(12), 41-55.

[8]. K. Al-Saadie, Corrosion inhibition of zinc in hydrochloric acid medium by thiourea andguanidine, *Iraqi J. Sci*., **2008**, 49(1), 29-34.

[9]. A. Khulood, Saleh, S. Khalil, Corrosion inhibition of zinc in hydrochloric acid solution using Ampicillin, *Iraqi J. Sci.,* **2014**, 55 (2A), 295-303.

[10]. Y. K. Agrawal, J. D. Talati, M. D. Shah, M. N. Desai, N. K. Shah, Schiff bases of ethylenediamine as corrosion inhibitors of zinc in sulphuric acid, *Corros. Sci*., **2004**, 46, 633-651.

[11]. R. T. Vashi, Krunal Desai, Hexamine as corrosion inhibitor for zinc in hydrochloric acid, *Der Pharma Chem.*,**2012**, 4(5), 2117-2123.

[12]. R. T. Vashi, D. Naik, Ethylamines as corrosion inhibitor for zinc in phosphoric acid, *Trans. SAEST*., **2006**, 41, 68-73.

[13]. P. B. Tandel, B. N. Oza, The effect of toluidine isomers on mild steel in aqueous solutions of ($HCl+HNO_3$) binary acid mixture, *Trans. SAEST,***2003**, 38(2), 75-78.

[14]. R. T. Vashi, V. A.Champaneri, Toluidine as corrosion inhibitors for zinc in sulphamic acid, *Ind. J. Chem. Tech.,* **1997**, 4, 180-184.

[15]. R. T. Vashi, S. A. Desai, P. S. Desai, Toluidines as corrosion inhibitors for zinc in nitric acid, *Ultra Chem.*, **2008**, 4(1), 27-34.

[16]. R. B. Patel, J. M., Pandya, K. Lal, Corrosion behaviour of A1-Cu in HC1 and its inhibition by toluidine isomers, *Trans. SAEST.*, **1982**, 17(4), 321.

[17]. M. N. Desai, S. S. Rana, Inhibition of the corrosion of copper in nitric acid: Aniline and other substituted aromatic amines, *Anti Corros. Meth.Mater*, **1973**, 20(6), 16-19.

[18]. E. G. Stroud, The quantatative removal of corrosion product from zinc, *J. Appl. Chem*., **1951**, 1, 93-95.

[19]. A. Y. El Etre, M. Abdallah, Z. E. El-Tantawy, Corrosion inhibition of some metal using *lawsonia* extract, *Corros. Sci*., **2005**, 47 (2), 385.

[20]. M. A. Deyas, Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution, *J. Ind. and Eng. Chem*., **2015**, 22, 384-389.

[21]. J. Halambek, A. Zutinic, K. Berkovic, *Ocimumbasilium* L. oil as corrosion inhibitor foraluminum in hydrochloric acid solution, *Int. J. Electrochem Sci*., **2013**, 8, 11201-11214.

[22]. G. R. Bruker, P. B. Phipps, Aliphatic amines as corrosion inhibitors for zinc in hydrochloric acid, *Corros. Chem. ACS.,* **1979**, 293.

[23]. I. N. Putilova, V. P. Barannik, S. A. Balezin, Metallic Corrosion Inhibitors, Pergamon Press, Oxford, **1960**, 30.

[24]. R. H. Thomson, Naturally Occurring Quinones, third ed., Academic Press, London, New York, **1971**, 74.

[25]. J. S. Martinez, M. Matikos-Hukovic, A nonlinear kinetic model introduced for the corrosion inhibitive properties of some organic inhibitors, *J. Appl. Electrochem.,* **2003**, 33, 1137-1147.

[26]. K. Orubite-Okorosoye, N. C. Oforka, Corrosion Inhibition of Zinc on HCl using Nypafruticans Wurmb Extract and 1,5 Diphenyl Carbazone. *J. Appl. Sci. Environ. Mgt.,* **2004**, 8, 57-61.

[27]. S. D. Shetty, P. Shetty, H. V. Nayak, Inhibition of mild steel corrosion in acid media by n-(2-thiophenyl)-n/-phenyl thiourea., *J. Chilean Chem. Soc.,* **2006**, 51, 849-853.

[28]. G. Mu, X. Li, G. Liu, Synergistic inhibition between 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid, *Corros. Sci.,* **2005**, 47, 1932.

[29]. T. T. Bataineh, M. A. Al-Qudah,, E. M. Nawafleh, N. A. F. Al Rawashdeh, Sinapisalba extract as green corrosion inhibitor for aluminium in alkaline media, *Int. J.Electrochem.Sci.,* **2014**, 9, 3543-3557.

[30]. Zarrouk, B. Hammouti, H.Zarrok, M. Bouachrine, K. F. Khaled, S. S. Al-Deyab, Corrosion inhibition of copper in nitric acid solutions using a new triazole derivative, *Int.J. Electrochem. Sci.,* **2012**, 7(1), 89-105.

[31]. T. Ibrahim, H. Alayan, Y. Al Mowaqet, The effect of Thyme leaves extract on corrosion of mild steel in HCl, *Prog. Org. Coat.,* **2012**, 75, 456.

[32]. D. Agrawal, K. D. Gupta, K. K. Saxena, Thermodynamics and equilibrium study of the formation of binary and tertiary complexes of Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} with (DL) 2,5 Diamino -1-pentanoic acid as secondary ligand and 2',2'-Biperidine (2',2'-Bipy) as primary ligand, *Trans. SAEST,* **2003**, 38, 111-114.

[33]. R. M. Issa, A. Z. El-Sonbati,A. A. El-Bindary, H. M. Kera, Polymer complexes XXXIV. Potentiometric and thermodynamic studies of monomeric and polymeric complexes containing 2-acrylamidosulphadiazine., *Eur. Polym. J.,* **2002**, 38(3), 561-566.

[34]. M. Muthukumar, V. Chandrasakaran, *Oscimum sanctum* as corrosion inhibitor for mild steel corrosion in phosphoric acid medium, *Asian J. Chem.,* **2009**, 21(1), 421-432.

[35]. E. E. Ebenso, Effect of methyl red and halide ions on the corrosion inhibition of aluminium in H_2SO_4, Part 2; *Bull. Electrochem.,* **2004**, 20, 551.

[36]. M. A. Quraishi, F. A. Ansari, D. Jamal, Thiourea derivatives as corrosion inhibitors for mild steel in formic acid, *Material Chem. And Phy.,* **2003**, 77, 687-690.

[37]. W. Li, X. Zhao, F. Liu, B. Hou, Investigation on inhibition behavior of S- triazole-derivatives in acidic solution, *Corros. Sci.,* **2008**, 50, 3261- 3266.

[38]. A. M. Shah,A. A. Rahim, S. A. Hamid, S. Yahya, Green inhibitors for copper corrosion by mangrove tannin, *Int. J. Electrochem. Sci.,* **2013**, 8, 2140.

[39]. E.Khamis, M. A. Ameer, N. M. Al-Andis, G. Al- Senani, Effect of thiosemicarbazones on corrosion of steel in phosphoric acid produced by wet process, *Corrosion,* **2000**, 56, 127.

[40]. A. C. Souzac, J. E. Mayb, A. T. Machadoa, A. L. R. Tacharda, E. D. Bidoiac, Effect of temperature on the corrosion inhibition of iron base metallic glass alloy in neutral solutions, *Surf. Coat.Tech.,* **2005**, 75,190.

[41]. F. Ansfield, Corrosion Mechanism, Marcel Dekker, New York, **1987**, 119.

[42]. W. X. Dan, X. Bin, L. Yuanpeng, S. L. Shan, L. Chao, Corrosion control of copper in 3.5 wt. % NaCl solutions by Domperiodone: Experimental and theoretically study, *Corros. Sci.,* **2014**, 85, 77-86.