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O-Toluidine as Corrosion Inhibitor for Zinc in Sulphuric Acid Medium

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ABSTRACT: The inhibition of the corrosion of zinc in sulphuric acid solution by *o*-toluidine has been studied using weight loss, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopic (EIS) and SEM techniques. 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. *o*-toluidine showed maximum I.E. of 91.46% at 60 mM in 0.5 M H₂SO₄ acid at 301 K. The value of free energy of adsorption (ΔG_{ads}^0), heat of adsorption (Q_{ads}), energy of activation (E_a), enthalpy of adsorption (ΔH_{ads}^0) and entropy of adsorption (ΔS_{ads}^0) were calculated. The inhibition effect is discussed in view of *o*-toluidine molecules adsorbed on the metal surface and it obeys Langmuir adsorption isotherm. Polarization curve indicates that inhibitor act as mixed type. The results obtained showed that the *o*-toluidine could serve as an effective inhibitor for corrosion of zinc in sulphuric acid.

KEYWORDS: Zinc, H₂SO₄, *o*-Toluidine, Corrosion Inhibition, Weight loss, Polarization, EIS, SEM.

I. INTRODUCTION

The problem of corrosion is of considerable importance due to increase in uses of metals and alloys. Zinc metal has a number of characteristics that make it a well-suited corrosion protective coating for iron and steel products. Sulphuric acid (H₂SO₄) is a strong acid and is used as a cleaner for rust, algae and scale from condensers and cooling tower [1]. Sulphuric acid is a very important commodity chemical, and indeed a nation's sulphuric acid production is a good indicator of its industrial strength. Corrosion of zinc in various acid media was studied by different researchers [2-7]. Many workers [8-12] 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 *o*-toluidine for zinc in various concentration of H₂SO₄ medium by weight loss, effect of temperature, polarization, EIS and SEM techniques.

II. EXPERIMENTAL

2.1. 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 dm² were 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 H₂SO₄ purchased from Merck using double distilled water.

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2.2. 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 H₂SO₄ solution without and with different concentrations of *o*-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% BaCO₃ [13]. 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.

2.3. Temperature effect

To study the effect of temperature on corrosion of zinc in 0.1 M sulphuric acid, 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 3 h in absence and presence of three *o*-toluidine at 60 mM concentration. Attention is paid to compensate the evaporation loss of corrosive media. Wesley [14] and ASTM [15] pointed out that thermostatic control to within ± 1 °C usually be considered satisfactory. 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_{ads}⁰), enthalpy of adsorption (ΔH_a) and entropy of adsorption (ΔS_a) were calculated.

2.4. Potentiodynamic polarization measurements

For polarization study, metal specimens having as area of 1 cm² were immersed to 230 mL 0.1 M H₂SO₄ in absence and presence of *o*-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 were 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 (i_{corr}) and the corrosion potential (E_{corr}) [16]. Cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) were calculated from the software installed in the instrument.

2.5. Electrochemical Impedance Spectroscopy (EIS) measurements

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 (R_{ct}), and double layer capacitance (C_{dl}) were calculated. Impedance measurements were carried out both in the absence and presence of inhibitor.

2.6 Scanning electron microscope (SEM) study

The zinc specimen immersed in 0.1 M H₂SO₄ (blank) and containing 60 mM of *o*-toluidine as inhibitors for a period of one day at 298 K. After exposure, specimen was removed, rinsed with double distilled water, dried and observed in scanning electron microscope to examine the surface morphology. The SEM image of polished zinc specimen was also taken. The surface morphology measurements of zinc specimens were examined using JEOL-5610 LV (Made in Japan) computercontrolled SEM.

III. RESULTS AND DISCUSSION

The results were presented in Tables 1 to 6 and in Figures 1 to 8.

3.1. Weight loss experiments

The weight loss experiment was carried out in 0.1, 0.3 and 0.5 M H₂SO₄ solution containing 30, 40, 50 and 60 mM concentration of *o*-toluidine at 301±1 K for a exposure period of 24 h was investigated. Corrosion rate (C.R.) was calculated using following equation:

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

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

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

Where: W_u = Weight loss in absence of inhibitor, W_i = Weight loss in presence of inhibitor.

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

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

3.1.1. 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 *o*-toluidine was 87.24, 89.28 and 91.46 % with respect to 0.1, 0.3 and 0.5 M sulphuric acid concentration respectively [Table-1].

3.1.2. 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 *o*-toluidine in 0.5 M H_2SO_4 the I.E. was found to be 62.18, 69.72, 85.06 and 91.46 % correspond to 30, 40, 50 and 60 mM inhibitor concentration respectively [Table- 1].

Table 1 :Effect of H_2SO_4 concentration on corrosion rate (CR) and inhibitor efficiency (I.E.) of zinc metal having different concentration of *o*-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^2d	I.E. (%)	CR mg/dm^2d	I.E. (%)	CR mg/dm^2d	I.E. (%)
I	II	III	IV	V	VI	VII	VIII
Blank	-	1035.50	-	2880.84	-	6179.88	-
<i>o</i> -Toluidine	30	524.28	49.37	1229.83	57.31	2337.20	62.18
	40	387.00	62.57	918.41	68.12	1871.26	69.72
	50	219.00	78.85	498.17	82.72	923.27	85.06
	60	132.12	87.24	308.82	89.28	527.76	91.46

Table 2 :Inhibition efficiency (I.E.), Corrosion rate(p) and Surface coverage(θ) on zinc in 0.1 M H_2SO_4 for an immersion period of 24h at 301 ± 1 K.

Inhibitor	Inhibitor concentration (mM)	CR mg/dm^2d	$\log p$	I.E. (%)	Surface coverage (θ)	1- θ	$\log (\theta/1-\theta)$
I	II	III	IV	V	VI	VII	VIII
Blank	-	1035.50	3.02	-	-	-	-
<i>o</i> -Toluidine	30	524.28	2.72	49.73	0.50	0.50	-0.18
	40	387.00	2.59	62.57	0.63	0.37	0.22
	50	219.00	2.34	78.85	0.79	0.21	0.51
	60	132.12	2.12	87.24	0.87	0.13	0.83

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3.2. 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 H₂SO₄ in absence and presence of 30, 40, 50 and 60 mM inhibitor concentration for an immersion period of 3h. As the temperature increases the corrosion rate was increases while percentage of inhibition efficiency (I.E.) decreases. Corrosion rate was increase as 10594.08, 12399.60 and 14709.52 mg/dm²d corresponding to 313, 323 and 333 K respectively in 0.1 M H₂SO₄(Table-3). Corrosion loss increases with temperature may be due to the desorption of the adsorbed molecules inhibitor and/ or aggressive at higher temperature and thus exposing the fresh metal surface to further attack [17], which results in intensification of the kinetic of electrochemical reaction [18] and thus explains the higher corrosion rate at elevated temperature, The addition of *o*-toluidine in corrosive media indicates that as the temperature increases I.E. decreases, e.g. in 0.1 M H₂SO₄ at 60 mM inhibitor concentration, the I.E. for *o*-toluidine was 55.36, 38.33 and 32.12 % at 313, 323 and 333 K respectively.

The value of energy of activation (E_a) has been calculated with the help of Arrhenius equation [19].

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

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

Table 3: Temperature effect on corrosion rate activation energy and heat of adsorption for zinc in 0.1 M H₂SO₄ in absence and presence of *o*-toluidine for an immersion period of 3 h.

Inhibitor concentration (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	6398.88	39.71	9638.16	22.27	13222.64	10.10	31.36	- 69.55	- 83.73
40	5709.28	46.10	9585.12	22.69	11630.04	21.11	30.42	- 89.95	- 08.23
50	4991.92	52.88	8257.52	33.40	10487.84	28.70	31.85	- 67.70	- 19.66
60	4726.16	55.36	7646.80	38.33	9983.36	32.12	32.15	-58.13	- 24.38

3.3. Energy of activation (E_a)

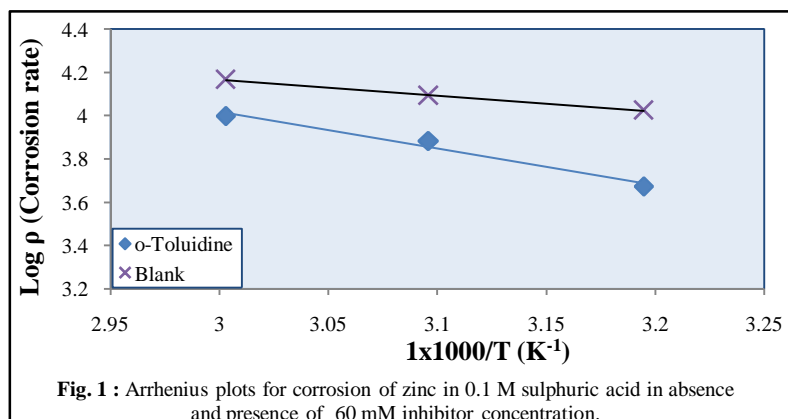
The mean " E_a " value calculated from equation (4) for zinc in 0.1 M H₂SO₄ was 14.25 kJmol⁻¹. A comparison of the values of the E_a for the corrosion process in inhibited (in the range 30.42 to 32.15 kJmol⁻¹) which indicates that the " E_a " values were higher in inhibited than in uninhibited acid (Table-3). The higher values of mean E_a , indicates physical adsorption of the inhibitors on metal surface [20]. The value of E_a calculated from the slop of Arrhenius plot (Fig. 1) and using equation (4) were almost similar.

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3.4. Heat of adsorption (Q_{ads})

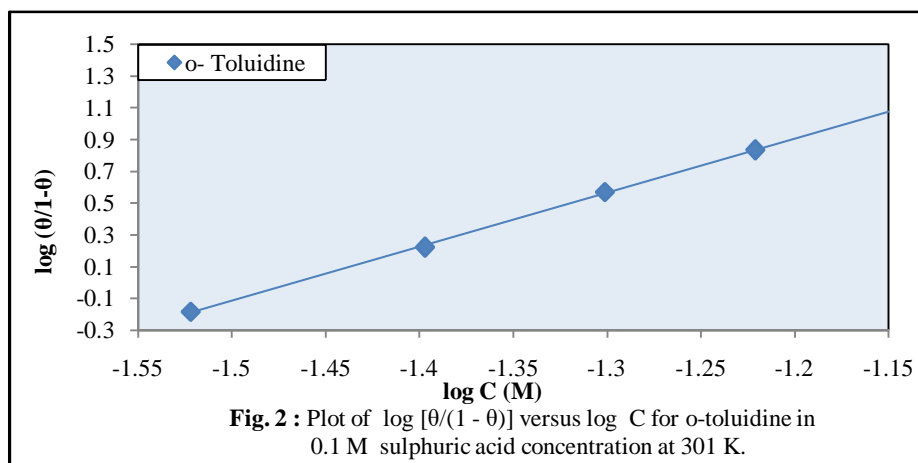
The values of heat of adsorption (Q_{ads}) were calculated by using the following equation [21]:

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

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-3 it was evident in all cases Q_{ads} values were negative and ranging from -08.23 to -89.95 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 [22].

3.5. Adsorption isotherm

The application of adsorption isotherms allowed to analyse the interaction mode in the inhibition process between adsorbent and adsorbed [23]. The Langmuir isotherm assumed that the adsorbed molecules occupy only one site and there was no interaction with other adsorbed molecules in metal surface [24]. A plot of inhibitor concentration $\log [\theta / (1 - \theta)]$ vs. $\log C$ for *o*-toluidine in 0.1 M H₂SO₄ was presented in Figure-2 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm [25].



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3.6. Free energy of adsorption (ΔG°_a)

The values of the free energy of adsorption (ΔG_a) [26] were calculated with the help of the following equation:

$$\log C = \log [(\theta/1 - \theta)] - \log B \quad \dots\dots\dots (6)$$

Where, $\log B = -1.74 - (\Delta G_a/2.303 RT)$, C is the inhibitor concentration and R is the gas constant. The mean ΔG°_{ads} value were found negative and ranging from -16.96 to -17.45 kJ mol⁻¹ suggest that the adsorption mechanism of *o*-toluidine on zinc in 0.1 M H₂SO₄ at the studied temperatures is physisorption with adsorptive layer having electrostatic character [27]. This is concluded on the fact that the values of ΔG°_{ads} -20 kJ mol⁻¹ are consistent with physisorption, while those around -40 kJ mol⁻¹ or higher are associated with chemisorptions [28].

3.7. Enthalpy of adsorption (ΔH°_{ads}):

The enthalpy of adsorption (ΔH°_a) [29] was calculated using the equation-7:

$$\Delta H^\circ_a = E_a - RT \quad \dots\dots\dots (7)$$

Results indicates that values of ΔH°_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°_a was positive and ranging from 14.39 to 40.95 kJmol⁻¹ indicating the endothermic nature of the reaction suggests that higher temperature favours the corrosion process [30]

3.8. Entropy of adsorption (ΔS°_{ads})

Entropy of adsorption (ΔS°_a) [31] were calculated using the equation-8,

$$\Delta S^\circ_a = \Delta H^\circ_a - \Delta G^\circ_a / T \quad \dots\dots\dots (8)$$

The entropy (ΔS°_{ads}) values were positive as 0.09 to 0.19 kJ mol⁻¹K⁻¹ confirming that the corrosion process is entropically favourable [32].

3.9 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-4). The result are in good agreement with the result obtain by Muthukumar and Chandrasekaran [33]. Corrosion rate constant 'K' increases with increases in concentration of acid (Table-4). The values of half-life (t_{1/2}) were calculated by [34] using the following equation-9:

$$t_{1/2} = 0.693 / k \quad \dots\dots (9)$$

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

Table-4 :Kinetic data for the corrosion of zinc in various concentration of sulphuric acid containing *o*- toluidine as inhibitor.

Inhibitor	Inhibitor concentration (mM)	Acid concentration					
		0.1 M		0.3 M		0.5 M	
		Rate constant	Half-life	Rate constant	Half-life	Rate constant	Half-life
		k x 10 ⁻³ day ⁻¹	t _{1/2} day ⁻¹	k x 10 ⁻³ day ⁻¹	t _{1/2} day ⁻¹	k x 10 ⁻³ day ⁻¹	t _{1/2} day ⁻¹
I	II	III	IV	V	VI	VII	VIII
Blank	-	15.9	43.45	45.07	15.37	99.97	6.93
<i>o</i> - Toluidine	30	6.50	105.57	18.84	36.78	35.24	19.66
	40	5.93	116.84	14.07	49.25	29.12	23.79
	50	5.05	137.20	7.646	90.63	14.38	48.19
	60	1.97	350.17	4.783	144.88	8.12	85.27

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3.10. Potentiodynamic polarization study

Potentiodynamic polarization curve of zinc in 0.1 M H₂SO₄ in absence and presence of 60 mM *o*-toluidine were shown in Fig-3 & Fig-4. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and percentage inhibition efficiency (I.E.) were given in Table -5. The curves show polarization of both, the cathodes as well as anodes (Fig. 3 & Fig. 4). I.E. calculated from corrosion current obtained by the extrapolation of the cathodic and anodic Tafel lines are given in Table-5. In almost all the cases, the I.E. from Tafel plots agree well (within $\pm 1\%$) with the values obtained from weight loss data.

Table5 : Potentiodynamic polarization data and Inhibition efficiency (I.E.) of *o*-toluidine as inhibitor for zinc in 0.1 M H₂SO₄.

System	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	Tafel slope (V / decade)			IE (%) Calculated from	
			Anodic (+ β_a)	Cathodic (- β_c)	β (V)	Weight loss method	polarization method
Blank	-1.094	2.2320	0.4133	0.2191	0.0622	-	-
<i>o</i> -Toluidine	-1.038	0.2746	0.1245	0.1474	0.0293	87.24	87.69

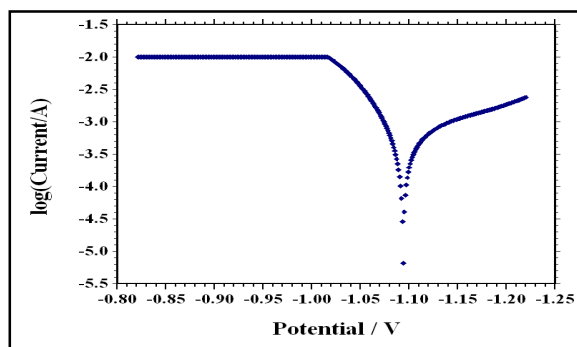


Fig. 3: Polarization curve for corrosion of zinc in 0.1 M sulphuric acid in absence of inhibitor.

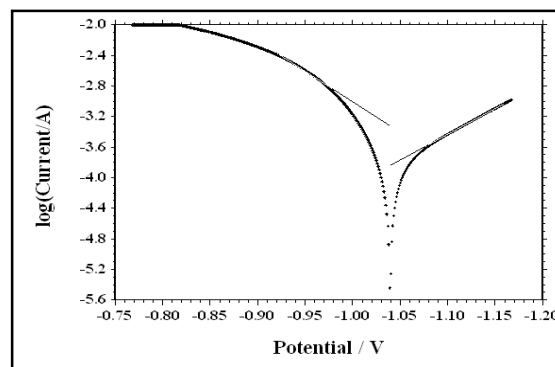


Fig. 4: Polarization curve for corrosion of zinc in 0.1 M sulphuric acid in presence of 60 mM *o*-Toluidine.

From Table-5, it was observed that the addition of *o*-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 [35,36]. In this study, the displacement of the E_{corr} was about 56 mV (Table -5), these result suggest that the *o*-toluidine should be considered as a mixed type of inhibitor. Inhibition efficiency (I.E.) from polarization study was calculated using following equation [37].

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

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

3.11. Electrochemical impedance spectroscopy (EIS) measurement

EIS technique was studied to investigate the growth of the film formed on metal surface by inhibitor. Corrosion of zinc in 0.1 M H₂SO₄ in presence of *o*-toluidine was investigated by EIS measurement at room temperature. Nyquist plots for zinc obtain in absence and presence of *o*-toluidine were shown in (Fig. 5 & Fig.6) and results are shown in Table-6.

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Table 6: EIS parameters for corrosion of zinc in 0.1 M H₂SO₄ containing *o*-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	-	-
<i>o</i> -Toluidine	210.0	18.05	88.11	87.24

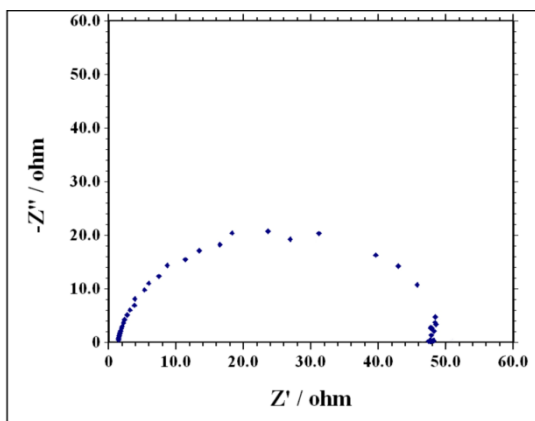


Fig. 5: Nyquist plot for corrosion of zinc in 0.1 M sulphuric acid in absence of inhibitor

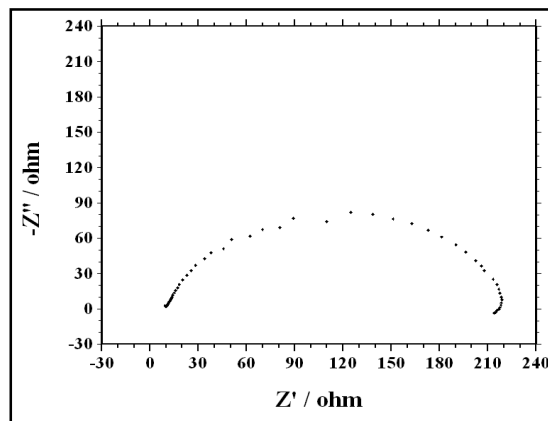


Fig. 6: Nyquist plot for corrosion of zinc in 0.1 M sulphuric acid containing 60 mM *o*-Toluidine.

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 [38].

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

Where 'f' is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [39].

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

$$I.E. (\%) = \frac{C_{dl}(uninhi.) - C_{dl}(inhi.)}{C_{dl}(uninhi.)} \times 100 \quad (12)$$

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 cm², at the same time it decreases the C_{dl} values from 151.84 to 18.05 μF / cm² which is due to the adsorption of inhibitor on the metal surface. 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} [40]. The results suggest that the inhibitor acts by the formation of a protective layer on the surface, which modifies the metal/solution interface. It was observed that from that the impedance diagram was almost

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semicircle in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion [41]. The semicircle nature of the plots indicates that the corrosion of zinc is mainly controlled by charge transfer process.

3.12. Scanning electron microscope (SEM) measurement

To understand the surface conditions of the metal specimen in the absence and presence of inhibitors SEM images are taken.

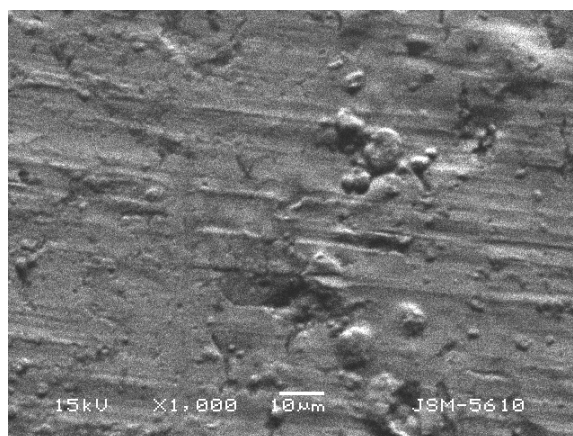


Fig. 7a: SEM images of polished zinc specimen. (X 1000)

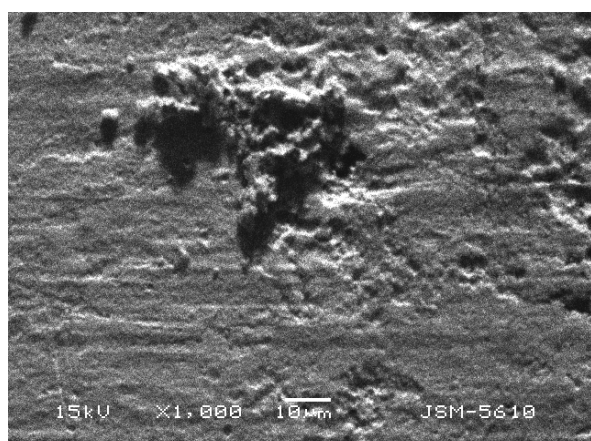


Fig. 7b: SEM micrograph of zinc surface exposed to 0.1 M sulphuric acid for 24 h. (X 1000)

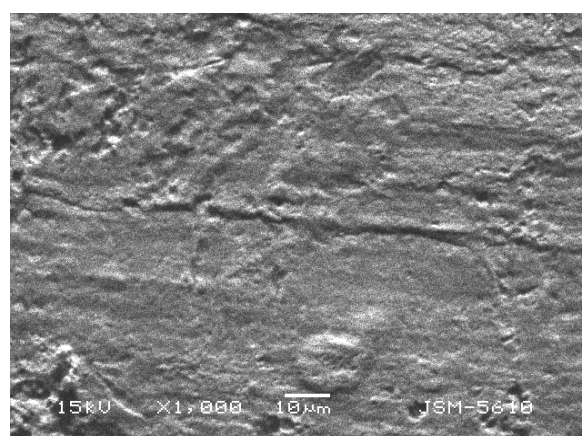


Fig. 7c: SEM micrograph of zinc surface exposed to 0.1 M sulphuric acid solution in presence of 60 mM of *o*-Toluidine for 24h (X 1000).

The morphology of the polished zinc plate is very smooth and shows no corrosion (Fig.7a) while zinc specimens dipped in a 0.1 M sulphuric acid in the absence of inhibitor (Fig.7b) is very rough and the surface was damaged due to metal dissolution. However, the presence of 60 mM *o*-toluidine as inhibitor suppresses the rate of corrosion and surface damaged has been diminished considerably (Fig.7c) as compared to the blank solution (Fig.7b) which suggest the formation of a protective inhibitor film at the zinc surface. As the inhibitor gets adsorbed by physisorption and binds on the metal surface, it shows less abrasion as compared to uninhibited conditions.

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3.13. Mechanism of corrosion of zinc

Corrosive attack of sulphuric acid on zinc which may be mainly due to the formation of HSO_4^- during the ionization of acid. However, inhibitors prevent the auto-catalytic cycle of the formation of HSO_4^- which results into inhibitor of the corrosion of zinc in sulfuric 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.



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



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



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



The following secondary reactions can also take place in acid solution:



As a result of the reaction, zinc during corrosion goes into the solution as ZnSO_4 which is highly soluble in aqueous media.

3.14. Mechanism of Corrosion Inhibition by *o*-toluidine

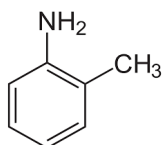


Fig. 8: Structure of *o*-toluidine

Methyl group has + R (Resonance) effect and + I (Inductive) effect which increases the basicity of a - NH_2 group. The pka value of *o*-toluidine is 4.39 which increases the basicity of *o*-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 *o*-toluidine. According to Mahida [42] position of methyl group present in molecule, which act as electron repelling group and provides more electron density on N-atom present on the ring and therefore increase I.E.

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IV. CONCLUSION

As acid concentration increases corrosion rate increases. At constant acid concentration, as inhibitor concentration increases corrosion rate decreases while I.E. increases. As temperature increases corrosion rate increases while I.E. decreases. Maximum I.E. of 91.46 % was obtained for *o*-toluidine at an optimum concentration of 60 mM. The values of E_a obtained in the presence of inhibitor was higher compared to the blank acid solution which indicates that the inhibitor was more effective at lower temperatures. The values of ΔG_{ads}° were negative, which reveals the spontaneous adsorption of inhibitor onto zinc metal surface. Plot of $\log [\theta / (1 - \theta)]$ vs. $\log C$ shows straight line with almost unit slope, which suggests that the inhibitor covers both anodic and cathodic regions through general adsorption following Langmuir isotherm. Polarization curves indicate that the *o*-toluidine acts as a mixed type of inhibitor.

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