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Anisidines as Corrosion Inhibitors for Zinc in Phosphoric Acid

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The corrosion of zinc in phosphoric acid has been studied at different acid concentrations, inhibitor concentrations and temperatures. Corrosion rate increases with the concentration of acid and the temperature. The inhibition efficiency (IE) of anisidines increases with the concentration of inhibitor. The inhibition efficiency decreases with the increase in concentration of acid. At 80 mM inhibitor concentration in 0.01 M H_3PO_4 acid at 301 K for 24 h immersion period, the inhibition efficiency decreases in the order: *m*-anisidine (98.7 %) > *o*-anisidine (97.3 %) > *p*-anisidine (96.0 %). As temperature increases, percentage of inhibition decreases. The plot of $\log\left(\frac{\theta}{(1-\theta)}\right)$ *versus* log C results in a straight line which suggests that the inhibitors cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. Galvanostatic polarization curves show the polarization of both the anode as well as cathode.

Key Words: Corrosion, Zinc, Phosphoric acid, Anisidines.

INTRODUCTION

Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow[1]. Phosphoric acid is a major chemical product, which has many important uses especially in the production of fertilizers. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors[2-4]. According to Hackerman *et al.*[5] the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of *p*-orbital free electron on the nitrogen atom of these compounds. Wang *et al.*[6] have studied the corrosion inhibition of zinc in phosphoric acid solution by 2-mercaptobenzimidazole. Sivaraju and Kannan[7] have studied the corrosion of mild steel in 1 N phosphoric acid with plant extract. In the present work, the corrosion of zinc by phosphoric acid containing isomer of anisidines has been reported.

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EXPERIMENTAL

To study the corrosion of zinc in phosphoric acid, weight loss method, temperature effect as well as polarization measurements have been used.

Rectangular specimens (4.50 cm × 2.03 cm × 0.17 cm) of zinc having an area of 0.205 dm^2 were cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M acid solutions (230 mL, each) with and without inhibitor at 301 ± 1 K for 24 h. After the test, specimens were cleaned by 10 % chromic acid solution having 0.2 % $BaCO_3$ for 2 min[8]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. Triplicate experiments were performed in each case and the mean value of the weight loss was reported in the form of corrosion rate as shown in Table-1. All chemicals used were of AR grade. The test solution was prepared in double distilled water.

TABLE-1
CORROSION RATE (CR) AND INHIBITION EFFICIENCY (IE) OF ZINC IN 0.01, 0.05, 0.10 AND 0.15 M H_3PO_4 ACID CONTAINING ANISIDINES AS INHIBITORS, IMMERSION PERIOD 24 h, TEMPERATURE 301 ± 1 K

System	Inhibitor concentration (mM)	Acid concentration							
		0.01 M		0.05 M		0.10 M		0.15 M	
		CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)
A	–	365.2	–	1887.6	–	3580.9	–	5205.2	–
B	20	43.8	88.0	1061.5	43.8	2463.8	31.2	3900.3	25.1
	40	34.1	90.7	637.9	66.2	2006.1	44.0	3656.8	29.7
	60	19.5	94.7	170.4	91.0	1441.3	59.7	2702.4	48.1
	80	9.7	97.3	73.0	96.1	852.1	76.2	2220.4	57.3
C	20	19.5	94.7	983.6	47.9	2337.2	34.7	3846.7	26.1
	40	14.6	96.0	574.6	69.6	1879.5	47.5	3359.8	35.4
	60	9.7	97.3	126.6	93.3	1334.2	62.7	2483.3	52.3
	80	4.9	98.7	34.1	98.2	633.0	82.3	2088.9	59.9
D	20	48.7	86.7	1154.0	38.9	2493.1	30.4	3997.7	23.2
	40	38.9	89.3	671.9	64.4	2259.3	36.9	3710.4	28.7
	60	24.3	93.3	185.0	90.2	1587.4	55.7	2843.6	45.4
	80	14.6	96.0	87.6	95.4	915.4	74.4	2303.2	55.8

A = H_3PO_4, B = H_3PO_4 + *o*-anisidine, C = H_3PO_4 + *m*-anisidine, D = H_3PO_4 + *p*-anisidine.

To study the effect of temperature on the corrosion rate of zinc in 0.05 M H_3PO_4, the specimens were immersed in 230 mL of corrosive solution at a temperature of 303, 313, 323 and 333 K for an immersion period of 3 h with and without inhibitors. inhibition efficiency, energy of activation (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG_a), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated and shown in Table-2.

For polarization study, metal specimens having an area of 0.026 dm^2 were immersed in 230 mL corrosive solution without and with 80 mM inhibitor concentration in

TABLE - 2

EFFECT OF TEMPERATURE ON CORROSION RATE (CR), INHIBITIVE EFFICIENCY (IE %), ENERGY OF ACTIVATION (E_a), HEAT OF ADSORPTION (Q_{ads}) AND FREE ENERGY OF ADSORPTION ($\Delta G°_a$) FOR ZINC IN 0.05 M H_3PO_4 ACID WITH AND WITHOUT INHIBITORS. INHIBITOR CONCENTRATION = 80 mM IMMERSION PERIOD = 3 h EFFECTIVE AREA OF SPECIMEN = 0.205 dm^2

System	Temperature (K)								Mean E_a from eqn. (1) (kJ mol^{-1})	E_a from Arrhenius plot (kJ mol^{-1})	Q_{abs} (kJ mol^{-1})			Mean value (kJ mol^{-1})		
	303		313		323		333				303-313	313-323	323-333	ΔG_a	ΔH_a	ΔS_a
	CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)	CR (mg/dm^2)	IE (%)								
A	832.6	–	993.3	–	1193.0	–	1314.7	–	12.7	15.3	–	–	–	–	–	–
B	19.5	97.7	29.2	97.1	53.6	95.5	68.2	94.8	34.8	34.7	-18.8	-36.6	-13.6	-25.9	29.5	0.18
C	4.9	99.4	14.6	98.5	34.1	34.1	43.8	96.7	60.2	60.8	-72.7	-57.1	-14.3	-27.9	84.2	0.37
D	34.1	95.9	48.7	95.1	68.2	68.2	97.4	92.6	29.4	29.0	-14.9	-13.6	-24.8	-24.3	25.6	0.16

A = H_3PO_4, B = H_3PO_4 + *o*-anisidine, C = H_3PO_4 + *m*-anisidine, D = H_3PO_4 + *p*-anisidine.

TABLE-3

POLARIZATION DATA AND INHIBITION EFFICIENCY (IE) OF ANISIDINES FOR ZINC IN 0.01 M H_3PO_4 AT 301 ± 1 K . INHIBITOR CONCENTRATION = 80 mM EFFECTIVE AREA OF SPECIMEN = 0.026 dm^2

System	E_{corr} (mV)	CD I_{corr} (mA/cm^2)	Tafel slope (mV/decade)		B (mV)	IE (%) from methods	
			Anodic	Cathodic		Weight loss	By polarization
			β_a	$-\beta_c$			
A	-940	0.560	88	117	22	–	–
B	-945	0.005	90	130	23	97.3	99.1
C	-950	0.004	170	145	34	98.7	99.3
D	-960	0.010	120	120	26	96.0	98.2

A = H_3PO_4, B = H_3PO_4 + *o*-anisidine, C = H_3PO_4 + *m*-anisidine, D = H_3PO_4 + *p*-anisidine, β_a = Anodic Tafel constant, β_c = Cathodic Tafel constant. CD = Corrosion current density from interception of anodic and cathodic lines.

0.01 M H_3PO_4. The test cell includes the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as platinum as an auxiliary electrode. The polarization study was done by using Potentio-Galvano-Scan (Weaving PGS 81) meter. 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})[9].

Inhibition efficiency has been calculated as follows:

$$\text{Inhibition efficiency}\,(\%) = \frac{(W_u - W_i)}{W_u} \times 100 \tag{1}$$

where, W_u = weight loss of metal in uninhibited acid and W_i = weight loss of metal in inhibited acid.

Energy of activation (E_a) has been calculated from the slope of log ρ *versus* 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation[10].

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \tag{2}$$

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

The value of heat of adsorption (Q_{ads}) were calculated by the following equation[10].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1 \times T_2}{T_2 - T_1}\right] \tag{3}$$

where, θ_1 and θ_2 [$\theta = (W_u - W_i)/W_i$] are the fractions of the metal surface covered by the inhibitors at temperature T_1 and T_2, respectively.

The values of the free energy of adsorption (ΔG_a) were calculated with the help of the following equation[11].

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \tag{4}$$

where, $\log B = -1.74 - (\Delta G_a/2.303\ RT)$ and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH°_a) and entropy of adsorption (ΔS°_a) are calculated using the equations[12].

$$\Delta H^\circ_a = E_a - RT \tag{5}$$

$$\Delta S^\circ_a = \Delta H_a - \Delta G_a/T \tag{6}$$

The values of the rate constant k were evaluated from the weight loss data and the values of half-life $t_{1/2}$ were calculated using following equation.

$$t_{1/2} = 0.693/k \tag{7}$$

RESULTS AND DISCUSSION

The results are presented in Tables 1-4 and in Figs. 1-4.

TABLE-4
KINETIC DATA FOR CORROSION OF ZINC IN VARIOUS CONCENTRATION OF PHOSPHORIC ACID CONTAINING ANISIDINES AS INHIBITORS. (FROM THE WEIGHT LOSS MEASUREMENTS) EFFECTIVE AREA OF SPECIMEN = 0.205 dm^2
IMMERSION PERIOD: 24 h, TEMPERATURE: 301 ± 1 K

Inhibitor	Inhibitor concentration (mM)	Acid concentration							
		0.01 M		0.05 M		0.10 M		0.15 M	
		Rate constant	Half-life	Rate constant	Half-life	Rate constant	Half-life	Rate constant	Half-life
		$k \times 10^{-3}$ (day^{-1})	$t_{1/2}$ (day^{-1})	$k \times 10^{-3}$ (day^{-1})	$t_{1/2}$ (day^{-1})	$k \times 10^{-3}$ (day^{-1})	$t_{1/2}$ (day^{-1})	$k \times 10^{-3}$ (day^{-1})	$t_{1/2}$ (day^{-1})
Blank	–	8.52	81.32	45.26	15.30	87.03	7.96	129.80	5.34
o-Anisidine	20	1.02	679.41	24.93	27.79	58.85	11.77	94.83	7.30
	40	0.79	877.21	14.91	46.47	47.65	14.54	88.64	7.81
	60	0.45	1540.00	3.96	175.00	34.01	20.37	64.74	10.70
	80	0.22	3150.00	1.69	410.05	19.96	34.71	52.88	13.10
m-Anisidine	20	0.45	1540.00	23.11	29.98	55.39	12.51	95.52	7.25
	40	0.34	2038.23	13.47	51.44	44.58	15.54	81.14	8.54
	60	0.22	3150.00	2.93	236.51	31.44	22.04	59.33	11.68
	80	0.11	6300.00	0.79	877.21	14.92	46.44	49.79	13.91
p-Anisidine	20	1.12	618.75	27.50	25.20	58.96	11.75	97.41	7.11
	40	0.90	770.00	15.71	44.11	53.39	12.93	89.87	7.71
	60	0.57	1215.78	4.30	161.16	37.24	18.60	67.90	10.20
	80	0.34	2038.23	2.05	338.04	21.47	32.27	54.96	12.60

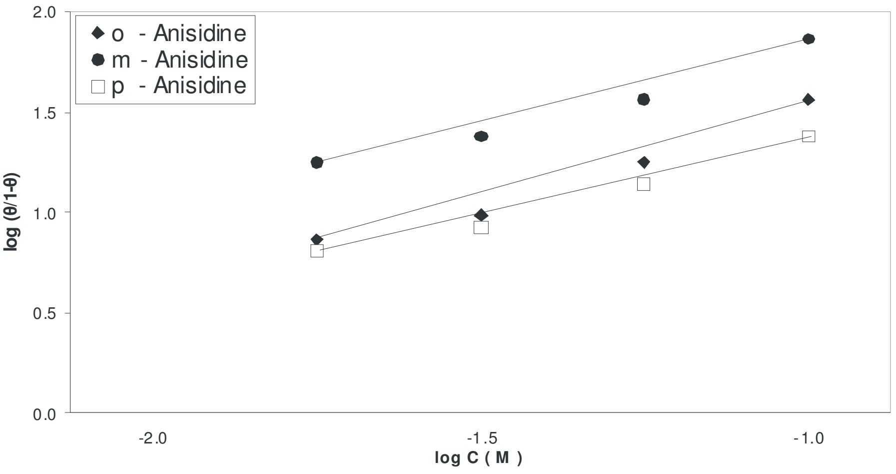


Fig. 1. Plot of $\log\left(\frac{\theta}{(1-\theta)}\right)$ *versus* log C for anisidines in 0.01 M phosphoric acid concentration

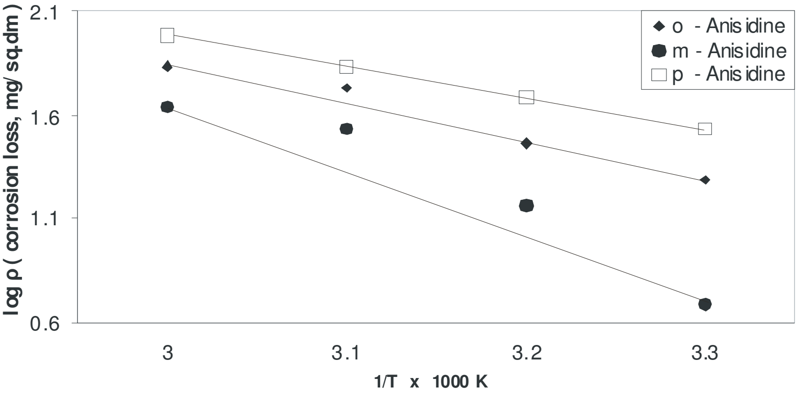


Fig. 2. Arrhenius plots for corrosion of zinc in 0.05 M phosphoric acid in presence of 80 mM inhibitor concentration

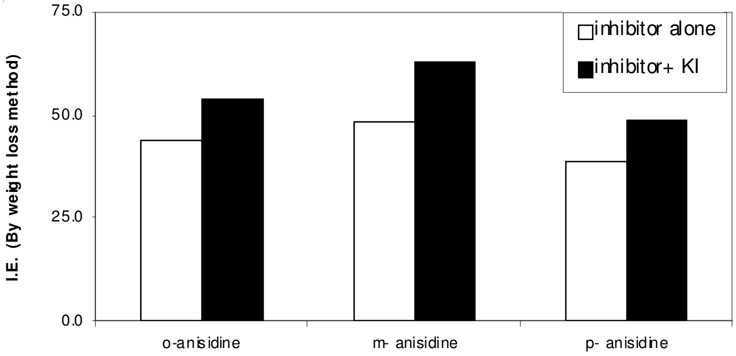


Fig. 3. Synergic effect of halides (30 mM KI) on inhibition of zinc in 0.05 M phosphoric acid with 20 mM inhibitor concentration at 301 ± 1 K

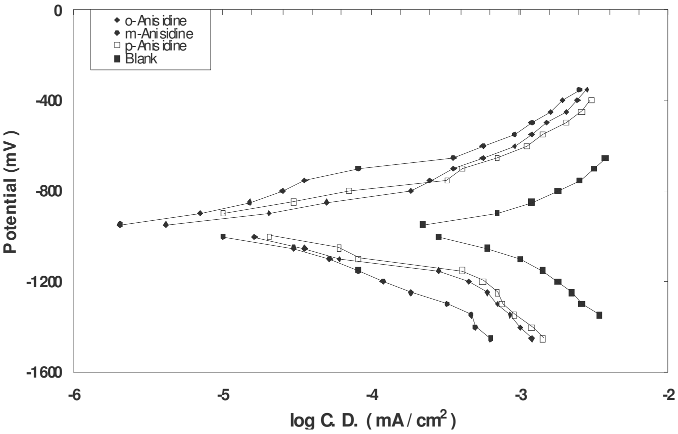


Fig. 4. Polarization curves of corrosion of zinc in 001 M phosphoric acid containing 80 mM inhibitors

Corrosion in acid: The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 365.2, 1887.6, 3580.9 and 5205.2 mg/dm^2 in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 concentrations, respectively for a period of 24 h at 301 ± 1 K as shown in Table-1.

Corrosion in presence of inhibitors: To assess their protective value, anisidines were added in 20, 40, 60 and 80 mM concentration in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 concentrations for 24 h duration period (Table-1).

Effect of inhibitor concentration: At constant acid concentration, the inhibition efficiency of the anisidines increases with the inhibitor concentration, *e.g.*, in case of *o*-anisidine in 0.01 M H_3PO_4 the inhibition efficiency was found to be 88.0, 90.7, 94.7 and 97.3 % with respect to 20, 40, 60 and 80 mM inhibitor concentration, respectively (Table-1).

Effect of acid concentration: At constant inhibitor concentration, the inhibition efficiency decreases with the increase in acid concentration. At 80 mM inhibitor concentration, the inhibition efficiency of *m*-anisidine is 98.7, 98.2, 82.3 and 59.9 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration, respectively (Table-1).

Effect of temperature: Corrosion rate increases with increase in temperature may be due to the desorption of the adsorbed inhibitor molecules and/or aggressive at higher temperature and thus exposing the fresh metal surface to further attack[13] which results in intensification of the kinetics of electrochemical reaction[14], this explains the higher corrosion rate at elevated temperature. At 80 mM inhibitor concentration in 0.05 M H_3PO_4, the inhibition efficiency was 95.9, 95.1, 94.3 and 92.6 % for *p*-anisidine at 303, 313, 323 and 333 K, respectively (Table-2).

Mean 'E_a' values calculated from eqn. 2 were found to be higher (from 29.4-60.2 kJ mol^{-1}) than that of uninhibited system (12.7 kJ mol^{-1}) (Table-2). This suggests that the presence of reactive centres on the inhibitor can block the active sites for corrosion, resulting in an increase in E_a[15]. The values of E_a calculated from the slope of Arrhenius plot (Fig. 2) and using eqn. 2 are almost similar. From Table-2, it is evident that in all cases, the Q_{ads} values are negative and ranging from -13.6 to -72.7 kJ mol^{-1}. Oguzie[16] explained that the negative values of Q_{ads} also signify that the degree of surface coverage decreased with rise in temperature.

The mean ΔG_a values are negative almost in all cases and lie in the range of -24.3 (*p*-anisidine) to -27.9 kJ mol^{-1} (*m*-anisidine). This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji[17]. The enthalpy changes (ΔH^o_a) were positive (in the range of 25.6-84.2 kJ mol^{-1}) indicating the endothermic nature of the reaction[18] suggesting that higher temperature favours the corrosion process. Adeyen[19] described that if the $\Delta H < 10$ kJ mol^{-1} the adsorption is probably physisorption and if the $\Delta H > 10$ kJ mol^{-1} values indicate that the anisidines strongly adsorbed on zinc is chemisorption. The entropy (ΔS^o_a) values are positive (in the range of 0.16-0.37 kJ mol^{-1}) confirming that the corrosion process is entropically favourable[20].

Kinetic parameters like rate constant (k) and half-life ($t_{1/2}$): Kinetic parameters like rate constant (k) and half-life ($t_{1/2}$) was calculated from the weight loss data and the results were presented in Table-4. The rate constant k decreases with increase in concentration of inhibitors whereas the half-life increases with the concentration of the inhibitor[21]. Higher the half-life period, higher will be the inhibition efficiency and lower the corrosion rate.

Synergistic effect of iodide ion: It has been reported that iodide ion is the most adsorbable of halide ions on steel[22] therefore; addition of iodide ion with an organic inhibitor enhances the inhibition efficiency. Hence an attempt was made to study the synergistic effect of iodide ion on various inhibitors. Since the compound is highly active, only lower concentrations were used for synergism study. The values of inhibition efficiency obtained by the weight loss method at 20 mM inhibitor concentrations without and with 30 mM KI were shown in Fig. 3.

Polarization behaviour: Anodic and cathodic galvanostatic polarization data for zinc in 0.01 M H_3PO_4 acid alone and containing 80 mM concentration of anisidines are shown in Table-3. The inhibition efficiency calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines. In almost all the cases, the inhibition efficiency from Tafel plots (Fig. 4) agree well (within ± 2 %) with the values obtained from weight loss data.

Mechanism of corrosion inhibitor: Generally, zinc dissolves in phosphoric acid. The reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (anodic reaction)} \tag{8}$$

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

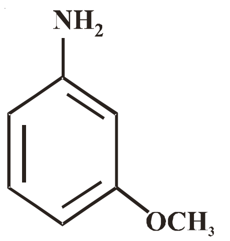
$$2H^+ + 2e^- \rightarrow 2H_{(ads.)} \text{ (cathodic reaction)} \tag{9}$$

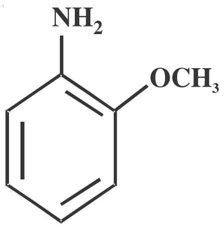
or
$$H + H_3O^+ + e^- \rightarrow H_2\uparrow + H_2O \tag{10}$$

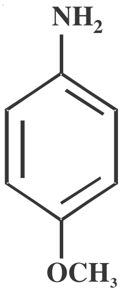
or
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{11}$$

The mechanism of corrosion inhibition is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when $\log\left(\frac{\theta}{(1-\theta)}\right)$ is plotted against log C, straight lines are obtained in case of all the three inhibitors studied (Fig. 1). This suggests that the inhibitors cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm. The order of inhibition efficiency in the increasing order was as follows: *p*-anisidine < *o*-anisidine < *m*-anisidine. This statement was supported by the work of Vashi *et al.*[23].

The delocalized π-electrons of these inhibitors facilitate its strong adsorption on the zinc surface leading to the outstanding corrosion inhibition. In addition, the oxygen of the methoxy group ($-OCH_3$) may facilitates the complexation to the zinc surface and helps to enhance the adhesion of anisidine coating to the zinc surface[24]. The presence of $-OCH_3$ group (*i.e.*, an electron donating effect) will enhance the electron density by their inductive or mesomeric effect[25].







m-anisidine	>	*o*-anisidine	>	*p*-anisidine
$pK_a = 4.20$		4.49		5.29
+ R Effect		+ R Effect		+R Effect
-I Effect		-I Effect		-I Effect

The three anisidines (M.W. 123.16) have the densities 1.092, 1.096 and 2.060 g/mL and molecular volumes correspond to *o*, *m* and *p*-anisidines are 1.873, 1.866 and 1.929×10^{-22} mL, respectively. A comparison of the inhibition efficiency of the anisidines and their molecular volume indicates that the compound with the lowest volume (*viz*., *m*-anisidine) shows better inhibitive power than *p*-anisidine with a larger volume. If it is assumed that the point of attachment to the metal is the nitrogen atom, then the molecules of *p*-anisidine will be adsorbed vertically and will therefore have lower covering power in spite of the larger volume. In the case of *o*- and *m*-anisidines the molecules are adsorbed in a slightly slanting position and therefore have more covering power. In such cases, the lower molecular volume is compensated for, by a large covering power due to molecular orientation[26].

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