

## N, N-DIMETHYLANILINE AS CORROSION INHIBITOR FOR ZINC IN SULPHURIC ACID MEDIUM

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### ABSTRACT

The inhibitive effect of N,N-Dimethylaniline (DMA) as corrosion inhibitor for zinc in 0.1, 0.3 and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions has been investigated by using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained reveal that inhibition efficiency (I.E.) increases with increase in concentration of inhibitors but decreases with increase in temperature. As inhibitor concentration increases corrosion rate decreases. The rate constant 'k' decreases while half-life 't<sub>1/2</sub>' increases with the increase in concentration of inhibitor. DMA showed maximum I. E. of 93.51 % at 60 mM in 0.5 M H<sub>2</sub>SO<sub>4</sub> acid at 301 K. The inhibition effect is discussed in view of DMA molecules adsorbed on the metal surface and it obeys Langmuir adsorption isotherm. Polarization curve indicates that inhibitor act as mixed type for zinc corrosion in sulphuric acid solutions.

**Keywords:** Zinc, H<sub>2</sub>SO<sub>4</sub>, N, N-Dimethylaniline, Corrosion, Polarization, EIS.

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## 1. INTRODUCTION

The problem of corrosion is of considerable importance due to increase in uses of metals and alloys. Zinc is an important metal with numerous industrial applications [1-2] and is mainly used for the corrosion sacrificial protection of steel [3-4]. Some industries practices involve the use of acid for scale removal, etching, pickling, oil wet cleaning and other applications [5-6]. The use of inhibitors has proven to be one of the best options towards the protection of metals against corrosion attack [7]. However, the preference for organic inhibitors has received wider acceptability because most of them are eco-friendly, less toxic, easily accessible and cost effective [8,9]. Possession of heteroatoms with high electron density, such as N, P, S and O in their molecular structures, suitable functional groups, pi-electron, steric factor, aromatic ring and high molecular mass have been identified as factors that can enhance the adsorption and hence the performance of organic compounds as corrosion inhibitors [10-12].

N, N-dimethyl aniline ( $C_8H_{11}N$ ) is a derivative of aniline obtained by replacing the two hydrogens with methyl groups. Aniline and N, N- Dimethylaniline was evaluated as corrosion inhibitor for the A<sub>3</sub> steel in 5 % HCl solution [13]. Successful application of aniline and some aniline derivatives for the inhibition of the corrosion of metals have been widely reported [14] and found that aniline (AL), *p*-toluidine (PTD), *p*-anisidine (PAD), *p*-phenitidine (PPD) and N, N-dimethylaniline (DMA) have strong corrosion inhibition efficiencies for mild steel in 3% HF which obeyed the trend, PAD > PPD > PTD > DMA > AL. DMA was found to exhibit maximum efficiency of 73.1 % while highest efficiency was reported for PAD. However, 1,4-dimethyl phenyl-N, N-dimethylanilinium bromide (a derivative of aniline was reported to exhibit efficiency up to 93 % for mild steel in solution of HCl [15]. Jakab et al. [16] studied inhibitory properties of N, N- dimethylaniline for copper in sulphuric acid solution. The obtained results showed that DMA is an anodic type inhibitor for copper corrosion in sulphuric acid solutions. Maximum I. E. was 43.5 % found at  $10^{-3}$  M DMA concentration. Talati and Pandya [17] studied anilines as corrosion inhibitor for aluminium-copper alloy in phosphoric acid. At 0.5 % inhibitor concentration in 0.033 M acid the inhibition efficiency of the inhibitors increases in the order: *o*-chloroaniline < N-N-diethylaniline < *p*-anisidine

< *p*-chloroaniline < *m*-chloroaniline < N-N-dimethylaniline < *m*-toluidine < methylaniline < *m*-anisidine < *o*-toluidine < *o*-anisidine < aniline < *p*-toluidine. Kumar and Yadav [18] studied N-N-dimethyl aniline as vapour phase corrosion inhibitor for mild steel under different atmospheric conditions and result shows 96.0 % inhibition efficiency. In spite of the established roles of corrosion inhibition attributed to aniline and aniline derivatives, literature is scanty on their application for the inhibition of the corrosion of zinc. Therefore, the present study is aimed at investigating the corrosion inhibition efficiencies of various concentrations of DMA in solution of H<sub>2</sub>SO<sub>4</sub>.

## 1. EXPERIMENTAL

### 2.1 Preparation of sample and solution

The zinc specimens with composition of 99.39 % Zn, 0.49 % Mn and 0.12 % Co were used for study. Metal coupons of dimension, 5.0 x 2.5 x 0.2 cm and effective area of 0.3013 dm<sup>2</sup> were used. The specimens were degreased by washing with doubled distilled water, rinsed in acetone and finally dried and weighted. Tetraoxosulphate (VI) acid was used as the corrodent. The test solution was prepared by dissolving various concentration of the inhibitor in 0.1, 0.3 and 0.5 M H<sub>2</sub>SO<sub>4</sub> respectively.

### 2.2 Weight loss measurements

For weight-loss measurement, the zinc coupons were each suspended in 230 mL of 0.1, 0.3 and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with different concentrations of DMA at 301± 1 K for 24h immersion period. After the test, the specimen was cleaned by using 10% chromic acid solution containing 0.2% BaCO<sub>3</sub> [19]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier and reweight.

To investigate the influence of temperature on corrosion of zinc, weight loss experiments were also carried out at 313, 323 and 333 K in 0.1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of 30, 40,50 and 60 mM inhibitor concentrations for an immersion period of 3h. From the weight loss data, Corrosion rate (C.R.) was calculated by using [20] following equation:

$$\text{C.R. (mg/dm}^2\text{d)} = \text{Weight loss (in milligrams)} / \text{Surface area of the metal in dm}^2 \times \text{Period of immersion in days.} \quad (1)$$

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 ‘ $\theta$ ’ of the zinc specimen for different concentration of  $H_2SO_4$  solution have been evaluated by weight loss experiments using the following equation:

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

### 2.3 Potentiodynamic polarization measurements

For polarization study, metal specimens having as area of  $1 \text{ cm}^2$  were immersed in 230 mL 0.1 M  $H_2SO_4$  in the absence and presence of DMA (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. The electrodes were immersed for 30 min to obtain steady state open circuit potential. In order to minimize ohmic contribution, the tip of lugging capillary was kept close to working electrode. Polarization curves are 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 ( $i_{\text{corr}}$ ) and the corrosion potential ( $E_{\text{corr}}$ ) [21]. Cathodic Tafel slope ( $\beta_c$ ) and anodic Tafel slope ( $\beta_a$ ) were calculated from the software installed in the instrument.

### 2.4 Electrochemical Impedance Spectroscopy (EIS) measurements

EIS measurements are made (using 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.

## 3. RESULT AND DISCUSSION

### 3.1 Weight loss experiments

### a) Effect of acid concentration

Results showed in Table 1 indicate that as the acid concentration increases corrosion rate and inhibition efficiency increases. Corrosion rate after 24 hours immersion period (and at 301 K) are 1035.50, 2880.84 and 6179.88 mg/dm<sup>2</sup>.d for acid concentrations of 0.1, 0.3 and 0.5 M. At constant inhibitor concentration, the Inhibition efficiency increases with increase in the concentration of the acid indicating that the inhibitor is an adsorption inhibitor [22]. At 60 mM inhibitor's concentration, the inhibition efficiencies of DMA were 85.89, 91.18 and 93.51 %, which corresponded to H<sub>2</sub>SO<sub>4</sub> concentrations of 0.1, 0.3 and 0.5 M respectively (Table 1). This reveals that the inhibition efficiency increases with increase in concentration of H<sub>2</sub>SO<sub>4</sub> and could be attributed to increase in the extent of protonation and hence adsorption [23].

### b) Effect of inhibitor concentration

At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while the inhibition efficiency increases. In 0.5 M H<sub>2</sub>SO<sub>4</sub> the inhibitor exhibited efficiencies of 68.28, 74.63, 82.02 and 93.51% at concentrations of 30, 40, 50 and 60 mM respectively (Table 1).

**Table 1.** Effects of H<sub>2</sub>SO<sub>4</sub> concentration on corrosion rate (C.R.) and inhibition efficiency (I.E) of zinc with different concentration of DMA

Inhibitor concentration (mM)	Acid concentration					
	0.1 M		0.3 M		0.5 M	
	CR (mg/dm <sup>2</sup> d)	I. E. (%)	CR (mg/dm <sup>2</sup> d)	I. E. (%)	CR (mg/dm <sup>2</sup> d)	I. E. (%)
Blank	1035.50	-	2880.84	-	6179.88	-
30	594.99	42.54	1506.96	47.69	1960.25	68.28
40	375.67	63.72	804.90	72.06	1567.83	74.63
50	310.33	70.03	580.77	79.84	1111.14	82.02
60	146.31	85.89	254.09	91.18	401.07	93.51

### c) Temperature effect

The addition of DMA in corrosive media indicates that as the temperature increases I. E. decreases, e.g. in 0.1 M H<sub>2</sub>SO<sub>4</sub>. At 60 mM inhibitor' concentration, observed efficiencies were 78.96, 71.09 and 63.53 % at 313, 323 and 333 K respectively. Increase in temperature was observed to lead to increasing corrosion rate and decreasing inhibition efficiency which implies that the mechanism of adsorption of the inhibitor is physisorption [24].

**Table 2.** Temperature effect on corrosion rate (C.R.) activation energy (E<sub>a</sub>) and heat of adsorption (Q<sub>ads</sub>) for zinc in 0.1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of DMA for an immersion period of 3h

Inhi. conc. (mM)	Temperature						'E <sub>a</sub> ' from eq. (4) (kJ mol <sup>-1</sup> )	'Q <sub>ads</sub> ' (kJ mol <sup>-1</sup> )	
	313 K		323 K		333 K			313- 323 K	323- 333 K
	CR mg/dm <sup>2</sup> d	I. E. (%)	CR mg/dm <sup>2</sup> d	I. E. (%)	CR mg/dm <sup>2</sup> d	I. E. (%)			
Blank	10594.08	-	12399.60	-	14709.52	-	14.25	-	-
30	6398.88	39.59	8390.24	32.33	10859.61	26.17	22.93	-26.56	-26.71
40	5177.52	51.12	7089.20	42.82	9664.72	34.29	27.07	-28.07	-23.31
50	3478.24	67.16	4965.12	59.95	7036.16	52.16	30.55	-26.22	-28.35
60	2309.92	78.96	3584.40	71.09	5363.36	63.53	36.60	-31.70	-30.83

### d. Energy of activation (E<sub>a</sub>)

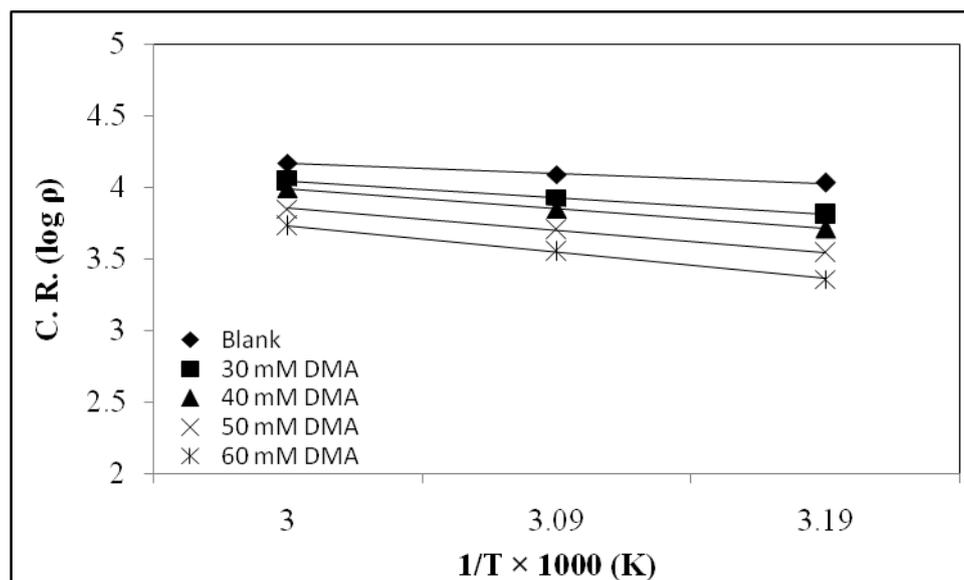
The value of energy of activation 'E<sub>a</sub>' has been calculated with the help of Arrhenius equation [25]:

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

Where, ρ<sub>1</sub> and ρ<sub>2</sub> are the corrosion rate at temperature T<sub>1</sub> and T<sub>2</sub> respectively.

The Arrhenius plots for the inhibition of the corrosion of zinc in solution of H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 1. From the results obtained, average activation energy was observed to ranging from 14.25 to 36.60 kJ mol<sup>-1</sup>. The value of E<sub>a</sub> calculated from the slop of Arrhenius plot (Fig. 1) and using eq. 4 were almost similar. The activation energy in the absence of the inhibitor was

the lowest which indicated that the corrosion of zinc in the studied medium is retarded by various concentrations of the inhibitor. The observed activation energies are within the range expected for the mechanism of physical adsorption. Hence the adsorption of the inhibitor is consistent with the transfer of charged from charged inhibitor to charged metal surface, which support physical adsorption mechanism.



**Fig.1.** Arrhenius plot for corrosion of zinc in 0.1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of N, N-Dimethylaniline

#### e) Heat of adsorption ( $Q_{ads}$ )

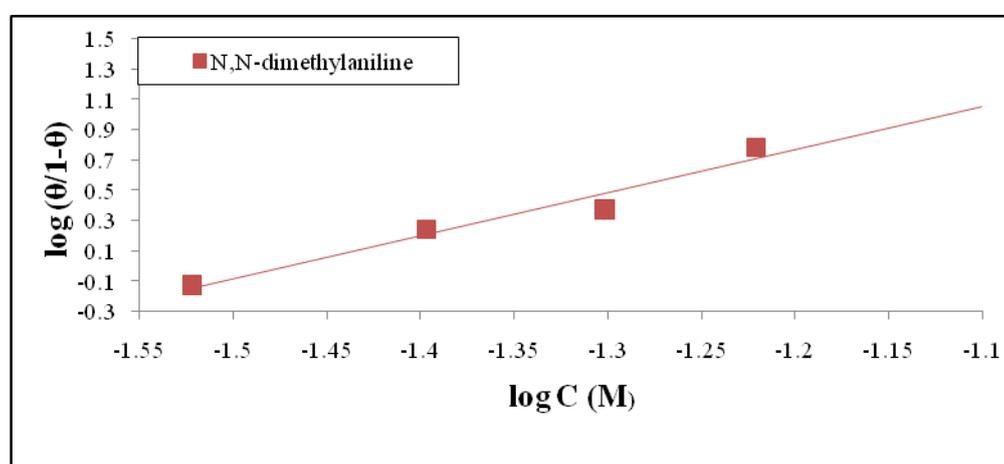
The values of heat of adsorption ( $Q_{ads}$ ) were calculated by using the following equation [26]:

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

Where,  $\theta_1$  and  $\theta_2$  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 -23.31 to -31.70 kJ mol<sup>-1</sup>. The negative values of  $Q_{ads}$  shows that the adsorption process and hence the Inhibition efficiencies decreases with rise in temperature supporting the physisorption mechanism [27].

#### f) Adsorption isotherm

Basic information on the interaction between the inhibitors and the zinc can be provided by the adsorption isotherm [10]. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The Langmuir isotherm assumed that the adsorbed molecules occupy only one site and there was no interaction with other adsorbed molecules in metal surface [28]. A plot of inhibitor concentration  $\log [\theta / (1 - \theta)]$  vs.  $\log C$  for DMA in 0.1 M  $H_2SO_4$  was presented in Figure 2 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm [29].



**Fig.2.** Langmuir adsorption isotherm for DMA of  $\log [\theta/(1 - \theta)]$  versus  $\log C$  in 0.1 M  $H_2SO_4$  at 301 K

### g) Free energy of adsorption ( $\Delta G_a^\circ$ )

Value of  $\Delta G_a$  was calculated with the help of the following equation [30];

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

Where,  $\log B = -1.74 - (\Delta G_a / 2.303 RT)$ , C is the inhibitor concentration and R is the gas constant. From the results, average values of  $\Delta G_{ads}$  were found to be negative (ranging from -18.19 to -20.74  $\text{kJ mol}^{-1}$ ) and were below the threshold value of -40 KJ/mol indicating that the adsorption of DMA on zinc surface is spontaneous and that the mechanism of physical adsorption is applicable [31] with adsorptive layer having electrostatic character [32]. The negative sign of  $\Delta G_{ads}^\circ$  ensures the spontaneity of the adsorption process and the value indicates that the inhibitor's molecules are physically adsorbed.

### ***h) Enthalpy of adsorption ( $\Delta H^{\circ}_a$ )***

$\Delta H^{\circ}_a$  was calculated using the following equation:

$$\Delta H^{\circ}_a = E_a - RT \quad (7)$$

Results indicates that values of  $\Delta H^{\circ}_a$  were positive and ranging between 20.16 to 34.33 kJ mol<sup>-1</sup> indicating the endothermic nature of the reaction which demonstrate that the dissolution reaction of zinc extremely slow [33] and suggests that higher temperature favours the corrosion process [34].

### ***i) Entropy of adsorption ( $\Delta S^{\circ}_a$ )***

$\Delta S^{\circ}_a$  was calculated using the following equation [35];

$$\Delta S^{\circ}_a = \Delta H^{\circ}_a - \Delta G^{\circ}_a / T \quad (8)$$

The entropy ( $\Delta S^{\circ}_a$ ) values were positive and ranging from 0.12 to 0.18 kJ mol<sup>-1</sup> K<sup>-1</sup> confirming that the corrosion process is entropically favourable [36].

### **3.2 Kinetic parameters: Rate constant (k) and Half-life ( $t_{1/2}$ )**

The values of half-life ( $t_{1/2}$ ) were calculated by using the following equation [37];

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

Where, 't' is time in hours and 'k' is rate constant. The value of rate constant 'k' were evaluated from the plots of log  $\rho$  versus time (h) (Fig. 3). The rate constant k decreases with increase in concentration of inhibitor whereas the half-life increases with concentration of inhibitor (Table 3). The results were in good agreement with the work of [38].

**Table 3.** Kinetic data for the corrosion of zinc in various concentration of H<sub>2</sub>SO<sub>4</sub> containing DMA as an inhibitor.

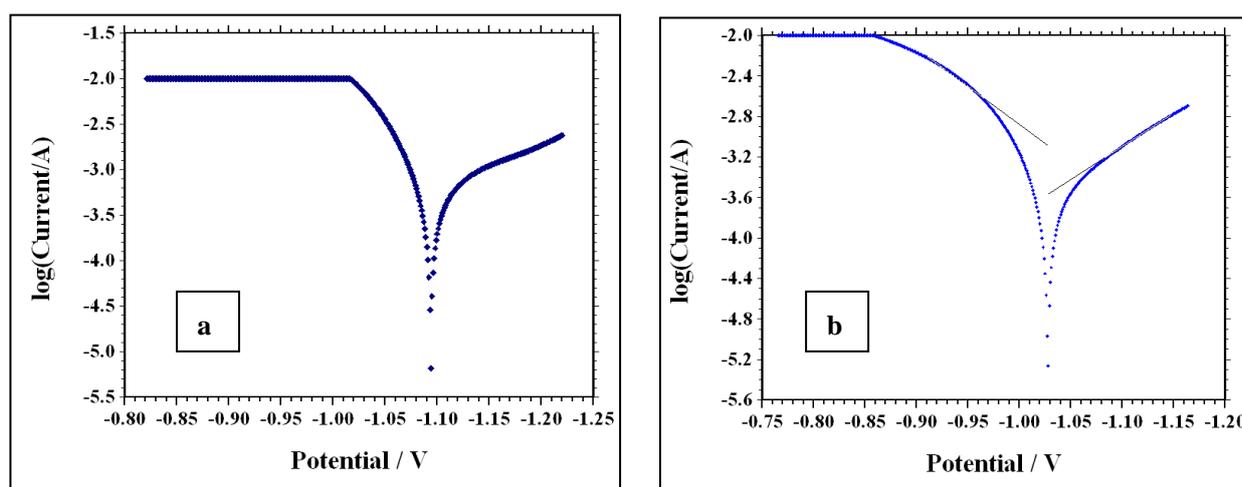
Inhibitor	Inhi. Conc. (mM)	Acid concentration (in Molar)					
		0.1		0.3		0.5	
		Rate const.	Half-life	Rate const.	Half-life	Rate const.	Half-life
		k x 10 <sup>-3</sup>	t <sub>1/2</sub>	k x 10 <sup>-3</sup>	t <sub>1/2</sub>	k x 10 <sup>-3</sup>	t <sub>1/2</sub>
		day <sup>-1</sup>	day	day <sup>-1</sup>	day	day <sup>-1</sup>	day
Blank	-	15.9	43.58	45.07	15.37	99.97	6.93
N, N-Di methyl aniline	30	7.20	95.37	23.18	29.89	30.48	22.73
	40	5.70	121.15	22.36	30.99	24.45	28.34
	50	3.98	174.12	8.93	77.57	20.83	33.26
	60	2.20	306.90	3.86	179.39	6.10	113.49

### 3.3 Potentiodynamic polarization study

Polarization measurements are suitable for monitoring the progress and mechanism of the anodic and cathodic partial reactions as well as identifying the effect of an additive on either partial reaction [39]. Polarization profiles for zinc in absence and presence of 60 mM DMA in 0.1 M H<sub>2</sub>SO<sub>4</sub> are presented Figure 3a and Figure 3b. Various electrochemical corrosion parameters like corrosion potential (E<sub>corr</sub>), corrosion current density (I<sub>corr</sub>), cathodic and anodic Tafel slopes (β<sub>c</sub>, β<sub>a</sub>), were drawn from the extrapolation of the Tafel lines and calculated % I. E. are summarized 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. The I. E. from Tafel plots agree well (within ± 8%) with the values obtained from weight loss data.

**Table 4.** Potentiodynamic polarization data for zinc in 0.1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of DMA

System	E <sub>corr</sub> (V)	I <sub>corr</sub> (mA /cm <sup>2</sup> )	Tafel slope (V / decade)			IE (%) Calculated from methods	
			Anodic (+β <sub>a</sub> )	Cathodic (-β <sub>c</sub> )	β (V)	Wt. loss	Polariz ation
			Blank	-1.094	2.2320	0.4133	0.2191
N, N-Dimethylaniline	-1.030	0.4911	0.1327	0.1520	0.0308	85.98	77.99



**Fig.3.** Polarization curves for corrosion of zinc in 0.1 M H<sub>2</sub>SO<sub>4</sub> (a) in absence and (b) In presence of 60 mM DMA

From Table 4, it was observed that the addition of DMA in acid solution indicates the significant decrease in corrosion current density ( $i_{\text{corr}}$ ) and decrease in corrosion rate with respect to blank. There is significant change in the anodic and cathodic slopes after the addition of the inhibitor. In general, an inhibitor is anodic or a cathodic if the variation of  $E_{\text{corr}}$  against the blank is higher or above than 85 mV [40], which suggest that the DMA should be

considered as a mixed type of inhibitor. Result from Table-4 indicates the displacement of  $E_{\text{corr}}$  was about 64 mV which suggest that the DMA should be considered as a mixed type inhibitor. Inhibition efficiency (I.E.) from polarization study was calculated using following equation [41].

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

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

### 3.4 Electrochemical impedance spectroscopy (EIS) measurements

EIS simultaneously provide details about the kinetics of electrode processes and surface properties of the investigated systems. The experimental data and calculated I. E. are summarized in the Table 5.

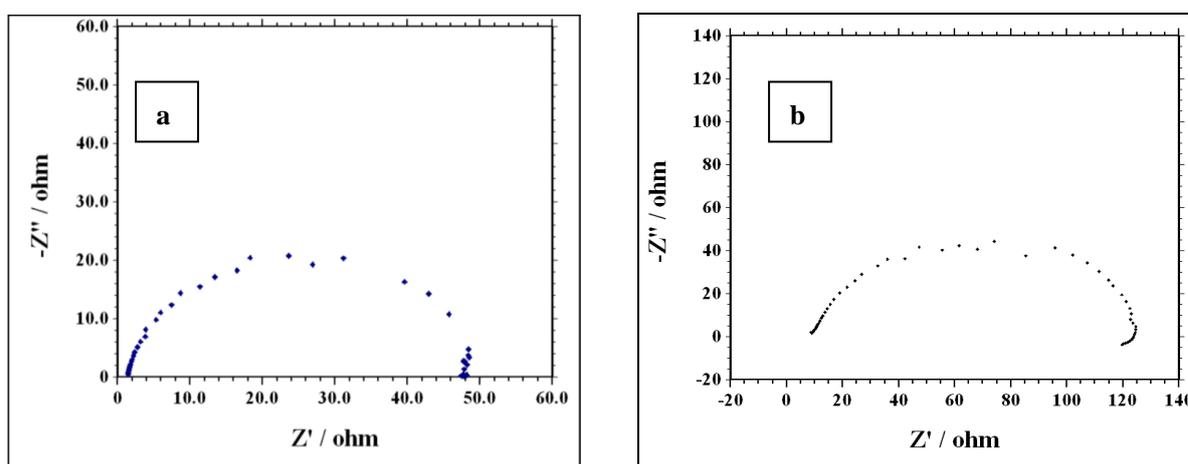
**Table 5.** EIS parameters for corrosion of zinc in 0.1 M  $\text{H}_2\text{SO}_4$  in absence and presence of 60 mM DMA

System	$R_{\text{ct}}$ ( $\Omega \text{ cm}^2$ )	$C_{\text{dl}}$ ( $\mu\text{F} / \text{cm}^2$ )	I.E. (%)	
			Calculated from	
			EIS	Wt. loss
Blank	49.5	151.84	-	-
N, N-Dimethylaniline	115.0	34.61	77.20	85.98

The electrochemical impedance spectra of zinc in absence and presence of 60 mM DMA in 0.1 M  $\text{H}_2\text{SO}_4$  at room temperature is presented as Nyquist plot in Figure 4a and Figure 4b respectively. The increased diameter of Nyquist plot in 0.1 M  $\text{H}_2\text{SO}_4$  in the presence of DMA indicated the corrosion inhibition of zinc. The high frequency capacitive loop is related to the charge transfer resistance ( $R_{\text{ct}}$ ). To calculate the double layer capacitance ( $C_{\text{dl}}$ ), the frequency at which the imaginary component of the impedance is maximum was found as presented in the following equation [42]:

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

Where 'f' is the frequency at the maximum height of the semicircle on the imaginary axis and  $R_{ct}$  is the charge transfer resistance [43].



**Fig. 4.** Nyquist plot for corrosion of zinc in 0.1 M  $H_2SO_4$  (a) in absence and (b) in presence of 60 mM DMA

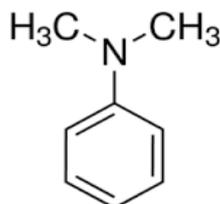
From EIS method I. E. was calculated using following equation:

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

The addition of inhibitor increases  $R_{ct}$  value from 49.5 to 115.0  $\Omega \text{ cm}^2$ , at the same time it decreases the  $C_{dl}$  values from 151.84 to 34.61  $\mu\text{F}/\text{cm}^2$  which is due to the adsorption of inhibitor on the metal surface. The increase in  $R_{ct}$  values was caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adherent film reducing the extent of dissolution [44]. However, the decrease in the  $C_{dl}$  values, which can result from a decrease in local dielectric constant and/or an increase in current density, the thickness of the electrical double layer, suggested by adsorption of the DMA at the metal/solution interface [45]. From the shapes of impedance diagram, mechanistic information can be derived. The observed deviations from perfect semicircles are often referred to the frequency dispersion of interfacial impedance [46]. This anomalous phenomenon is interpreted as reflecting inhomogeneity of electrode surfaces

arising from surface roughness or interfacial origin such as those found in adsorption processes.

### 3.6 Mechanism of corrosion inhibition by N,N-Dimethylaniline



**Fig.5.** Structure of N,N-dimethylaniline

N,N-Dimethylaniline (DMA) is a substituted derivative of aniline. It consists of a tertiary amine, featuring dimethyl amino group attached to a phenyl group. In DMA the amino hydrogens are replaced by two methyl groups. N,N-dimethylaniline there is no steric hindrance, so the lone pair is in the same plane as the benzene ring and undergoes resonance. Therefore, the lone pair on the tetramethyl derivative is more available and hence it is more basic so shows higher I.E. An electron releasing group (-CH<sub>3</sub>), that has plus inductive effect (+I) on aniline increases its basicity because it reduces the resonance of an NH<sub>2</sub> group. DMA is protonated in sulphuric acid forming aryl ammonium ions [47], which are preferentially oriented with the ammonium group to the metal surface inhibition effect, is due to their strong adsorption on the active corrosion sites or the deposition of corrosion product on the zinc surface.

## 4. CONCLUSION

As acid concentration increases corrosion rate increases. At constant acid concentration, as inhibitor concentration increases corrosion rate decreases while inhibition efficiency increases. The rate of corrosion decreased with inhibitor concentration and increased with temperature. DMA showed maximum inhibition efficiency of 93.51 % at an optimum concentration of 60 mM in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The rate constant 'k' decreases with increase in concentration of inhibitor whereas the half-life increases with concentration of inhibitor. The adsorption of DMA on zinc surface obeyed Langmuir adsorption isotherm. The addition of inhibitor leads to increase in activation energy showing that the inhibitor is being physically adsorbed on the

surface of the metal. The percentage of inhibition efficiency resulted from polarization and EIS measurements were in good agreement. A polarization curve indicates that the DMA act as mix type of inhibitor.

## 5. ACKNOWLEDGEMENTS

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