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Effect of Orthophenylenediamine on the Corrosion Inhibition of Brass in Nitric Acid Solution

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ABSTRACT: The inhibition effect of orthophenylenediamine (OPD) on the corrosion of brass in nitric acid solution has been investigated by weight loss, temperature effect, Potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) methods. Corrosion rate increases with the increase in acid concentration and temperature. The percentage of inhibition efficiency (I.E.) increases with increase in inhibitor concentration. Maximum I.E. was found 97 % in 0.1M HNO₃ with 20 mM inhibitor concentration. Adsorption of the inhibitor on the surface obeyed the Langmuir adsorption isotherm. Polarization measurement indicated that, the studied inhibitor act as a mixed type one. The results obtained from the different methods are in good agreement. The SEM of the brass surface revealed that the compound prevented from corrosion by adsorption on its surfaces.

KEYWORDS: Brass, HNO₃, Corrosion inhibition, Weight loss, Polarization, EIS , SEM.

I. INTRODUCTION

Copper and its alloys are widely used in industry especially in heating and cooling system because of their excellent electrical and thermal conductivity [1]. Brass is broadly used as tubing material for condensers and heat exchangers in various cooling water system [2-4]. Among the corrosive media, the nitric acid is recognized as a strong oxidizing agent that is able to corrode copper and its alloys quite easily. In this respect, the corrosion of brass in this environment has been subjected to extensive researches [5-9]. Much more research works are concentrated on the studies of the relationship between structural characteristics of the organic compounds and their inhibiting effects [10,11]. It had been suggested that the most effective factors of which they can offer special active electrons or vacant orbital to donate or accept electrons for the inhibiting effects are: the electronegative atoms (such as, N, S, P, O, etc.) [12] and the plane conjugated systems including all kinds of aromatic cycles [10-13]. In many cases, the inhibition is related to adsorption of the inhibitor on the metal surface forming a barrier layer which separates the metal from the corrosive media. According to the type of inhibitor species and the nature of metal and alloy, adsorption may be chemical or physical adsorption [14-17]. Orthophenylenediamine (OPD), a non-ionic surfactant has been used as inhibitor for the corrosion of carbon steel in HCl [18,19]. In the present work, inhibitive action of OPD on the corrosion behaviour of Brass in HNO₃ acid media is measured. Corrosion inhibition is investigated by using weight loss, potentiodynamic polarization and EIS methods and their results are compared. Also, the thermodynamic functions for the adsorption process was tested using Langmuir isotherm.

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II. EXPERIMENTAL

2.1. Preparation of sample and solution

Weight loss measurements were carried out using brass specimens with chemical composition 60.73 % Cu, 39.21 % Zn, 0.01 % Fe, 0.02 % Sn and 0.04 % Pb. The brass specimens of size 4.4 x 2.0 x 0.181 cm are used. The specimens are cleaned by washing with distilled water, degreased by acetone, washed again with doubled distilled water and finally dried and keep in dessicator till use. The corrosive solution was prepared by diluting analytical grade of HNO₃ purchased from Merck using double distilled water. For present study 0.1, 0.25, 0.5 and 1.0 M HNO₃ are prepared. Inhibitor concentration are taken as 5, 10, 15 and 20 mM

2.2. Weight loss measurements

For weight-loss measurement, the brass specimens having an area of approximately 0.206 dm² are each suspended completely in 0.25, 0.5 and 1.0 M HNO₃ solution without and with different concentrations of OPD using glass hooks at 301± 1 K for 24 h. The volume of solution was kept 230 ml. The coupons are retrieved after 24 h, washed with distilled water, dried well and reweighed on electronic balance. From the weight loss data, corrosion rate (CR) are calculated.

2.3. Temperature effect

To study temperature effect, brass coupons are completely immersed in 230 ml of 0.1 M HNO₃ solution with and without different *o*-phenylenediamine concentrations at 313, 323 and 333 K for 2 h. From the corrosion data inhibition efficiency (I.E.), activation energy (E_a) and heat of adsorption (Q_{ads}), free energy of adsorption (ΔG⁰_{ads}), entropy of adsorption (ΔS⁰_{ads}) are calculated.

2.4. Potentiodynamic polarization measurements

Both the potentiodynamic and EIS measurement are carried out using CHI608C –series, U.S. Model with CH-instrument. For polarization study, metal specimens are immersed without and with OPD in 0.1 M HNO₃ solution. In the electrochemical cell, brass specimens having an area of 1 cm² was used as a working electrode, Ag/AgCl electrode as a reference electrode and platinum electrode as an auxiliary electrode and allowed to establish a steady-state open circuit potential (OCP) for approximately 25 min. The polarization curves are plotted with current Vs potential. An anodic and cathodic polarization curve gives anodic and cathodic Tafel lines corresponding. The intersect point of Tafel lines gives the corrosion potential (E_{corr}) and corrosion current (i_{corr}) [20]

2.5. Electrochemical Impedance Spectroscopy (EIS) measurements

EIS studies are carried out in the same set up using Potentiodynamic polarization measurements described above. EIS measurements are carried out at steady state OCP. A small amplitude of 5 mV sinusoidal AC voltage, in wide frequency range of 0.1 to 105 Hz was applied over the system. A graph was drawn by plotting real impedance (Z') and imaginary impedance (-Z'') . From the Nequist plots, the charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) are calculated in absence and in presence of inhibitor.

2.6. Scanning electron microscope (SEM) study

The surface morphology measurement of brass specimens are examined using FEI, Model- Inspect computer controlled SEM.

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III. RESULTS AND DISCUSSION

3.1. Weight loss experiments

The weight loss experiments are carried out in 0.1, 0.25, 0.5 and 1.0 M HNO₃ solution without and with 5, 10, 15, 20 mM concentration of *o*-phenylenediamine at 301±1 K for a exposure period of 24 h and corrosion rate is calculated from the weight loss data using following equation.

$$CR \text{ (mg/dm}^2\text{d)} = \frac{\text{Weight loss (gm)} \times 1000}{(\text{metal surface area})\text{dm}^2 \times \text{day}} \quad (1)$$

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

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

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

The surface coverage (θ) data are very useful while discussing the adsorption characteristics. The value of (θ) can be used to determine the thermodynamic parameters and the mode of the adsorption process. The degree of surface coverage (θ) of the brass specimen for different inhibitor concentration in HNO₃ solution have been evaluated by weight loss experiments using the following equation,

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

Table 1: Effect of HNO₃ concentration on corrosion rate (CR) and inhibition efficiency (IE) of brass having different concentration of *o*-phenylenediamine.

Inhibitor concentration (mM)	Acid concentration							
	0.1 M		0.25 M		0.5 M		1.0 M	
	CR (mg dm ⁻² d ⁻¹)	I.E. (%)	CR (mg dm ⁻² d ⁻¹)	I.E. (%)	CR (mg dm ⁻² d ⁻¹)	I.E. (%)	CR (mg dm ⁻² d ⁻¹)	I.E. (%)
Blank	1820.39	-	6577.67	-	9393.20	-	15902.91	-
5	163.11	91.04	592.17	90.99	3467.77	63.08	8478.83	46.68
10	125.39	93.11	525.63	92.00	2713.88	71.11	6725.23	57.71
15	98.49	94.59	399.87	93.92	2227.59	76.29	5461.64	65.66
20	47.15	97.41	216.21	96.71	1887.46	79.91	4920.19	69.06

3.1.1 Effect of acid concentration

Results showed in Table 1 indicates that as the concentration of acid increase corrosion rate increases while I.E. decreases.

3.1.2 Effect of inhibitor concentration

At constant acid concentration, I.E. increases with increase in OPD concentrations. The maximum I.E. (97.41%) has been observed at 20 mM inhibitor concentrations in 0.1 M HNO₃ at 24 h at 301 K. At constant inhibitor concentration, the I.E. was decreases as the acid concentration increases (Table 1). The results indicates that with increase in inhibitor concentration from 5 to 20 mM the corrosion rate was decreases from 163.11 to 47.15 mg/dm²d in 0.1 M HNO₃ (Table 1 and Figure 1).

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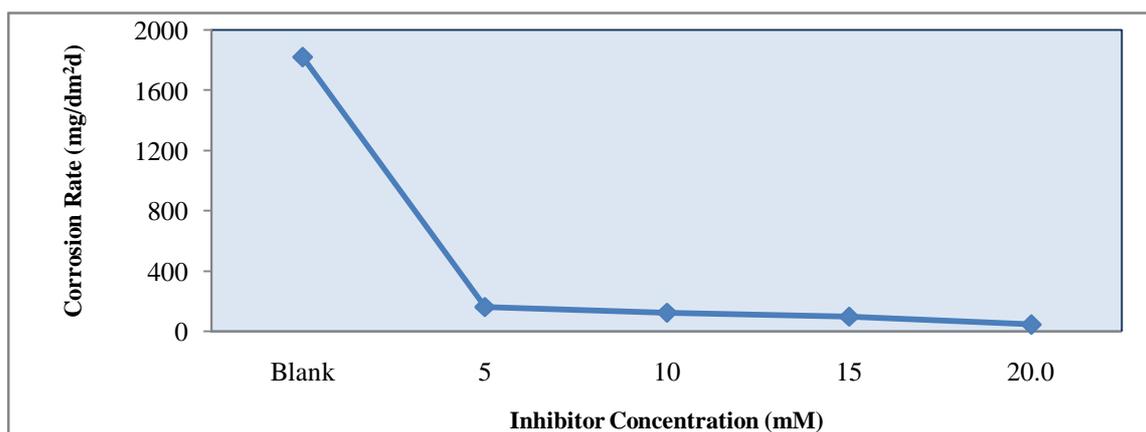


Fig.1: Corrosion rate of brass in 0.1 M HNO₃ solution in presence of different concentration *o*-phenylenediamine for an immersion period of 24h.

Table 2: Corrosion rate ($\log \rho$) and surface coverage (θ) of brass in absence and presence of OPD in 0.1 M HNO₃ for an immersion period of 24h at 301 ± 1 K.

Inhibitor	Inhibitor Concentration (mM)	C.R.(ρ) (mg dm ⁻² d ⁻¹)	$\log \rho$	I.E. (%)	Surface coverage (θ)	C/ θ
Blank	0	1820.39	3.26	-	-	-
<i>o</i> -phenylene diamine	5	163.11	2.21	91.04	0.91	5.49
	10	125.39	2.10	93.11	0.93	10.75
	15	98.49	1.99	94.59	0.95	15.79
	20	47.15	1.67	97.41	0.97	20.62

3.2. Effect of Temperature

The importance of temperature variation in corrosion study involving the use of inhibitors is to determine the mode of inhibitor adsorption on the metal surface. To investigate the influence of temperature on corrosion of brass in HNO₃, the weight loss experiments are carried out at temperature 313, 323 and 333 K in 0.1 M HNO₃, without and with OPD for an immersion period of 2 hr. The results presented in Table 3 shows that as temperature increases corrosion rate increase while I.E. was decrease. The maximum I.E. (89.10 %) was found at 20 mM inhibitor concentration at 24 h at 313 K. At elevated temperature (333 K), the I.E. reduces to 80.23 %. With an elevation in temperature, due to the thermal agitation, the desorption process of the adsorbed constituents of the inhibitor increases, leading to a decrease in the I.E. (Table 3). The value of energy of activation (E_a) has been calculated with the help of following Arrhenius equation [21].

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

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

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Table 3: Temperature effect on corrosion rate (CR), activation energy (E_a) and heat of adsorption (Q_{ads}) for brass in 0.1M HNO_3 in absence and presence of *o*-phenylenediamine for an immersion period of 2h.

Inhibitor concentration (mM)	Temperature						Mean E_a From Equation (4) ($kJmol^{-1}$)	Qads ($kJ mol^{-1}$)	
	313 K		323 K		333 K			313-323 K	323-333 K
	CR $mg dm^{-2}d^{-1}$	I. E. (%)	CR $mg dm^{-2}d^{-1}$	I. E. (%)	CR $mg dm^{-2}d^{-1}$	I. E. (%)			
Blank	2213.52	-	3436.92	-	4660.2	-	32.11	-	-
5	711.24	67.87	1671.00	51.38	2360.52	49.35	51.05	-60.00	-3.59
10	572.28	74.15	1386.72	59.65	1971.96	57.69	52.94	-53.84	-7.40
15	476.64	78.47	920.76	73.20	1443.12	69.03	47.77	-22.78	-17.40
20	241.32	89.10	769.32	77.61	1179.84	74.68	67.85	-74.18	-9.81

Results given in Table-3, indicates that the mean values of E_a are found higher in inhibited acid ranging from 47.77 to 67.85 $kJ mol^{-1}$ than the E_a values for uninhibited acid 32.11 $kJ mol^{-1}$. The higher values of E_a indicate physical adsorption of the inhibitor on the metal surface and the adsorption of inhibitor causes an increase in the E_a of the process [22]. This means that the adsorption of inhibitor on brass electrode surface leads to the formation of barrier layer that retards the metal activity in the electrochemical reactions of corrosion. Results of Table-3 indicates that as temperature increases, rate of corrosion increase while percentage of I.E. decreases. The value of E_a are also calculated from the slope of the Arrhenius plot of $\log p$ versus $1/T \times 1000$ (Fig.2). The mean value of E_a calculated from equation and from the slope of the Arrhenius plot (Fig.2) was found almost similar value ($\pm 1.0 kJ mol^{-1}$).

The values of heat of adsorption (Q_{ads}) are calculated by following equation [23].

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

Where, θ_1 and θ_2 ($\theta = W_u - W_i / W_u$) are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. From Table 3, it is evident that in all cases, the Q_{ads} values are negative and ranging from -3.59 to -74.18 $kJmol^{-1}$. 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 [24].

3.3. Adsorption isotherm

Adsorption isotherm study was conducted to investigate the interaction between the metal and inhibitor as well as the equilibrium of the adsorption. The process of adsorption occurs when liquid or gas accumulates on the surface of a solid or liquid, forming a molecular or atomic film. Basic information on the interaction between inhibitors and a metal surface can be provided using the adsorption isotherm [12]. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion. The adsorption of an organic adsorbate at the metal-solution interface can occur as a result of the substitution adsorption process between organic molecules presented in the aqueous solution (Org(sol)), and the water molecules previously adsorbed on the metallic surface ($H_2O(ads)$) [25,26].



Where Org(sol) and Org(ads) are the organic species in the bulk solution and those adsorbed on the metallic surface, respectively. $H_2O(ads)$ is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic adsorbate. The surface coverage ' θ ' suggests that a chemical bond is formed between the metal atoms and the inhibitor molecules. In order to obtain the adsorption isotherm, the degree of surface coverage ' θ ' for different concentrations of an inhibitor in 0.1 M HNO_3 solution has been evaluated from

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weight loss method. Langmuir isotherm was given by a plot of C/θ Vs C as shown in Figure 5 to be linear with slope value equal to unity indicates that the inhibitor obey Langmuir adsorption isotherm. It was found that the best suitable adsorption isotherm for the studied inhibitor on the brass surface is the Langmuir equation [27] which was defined as follows:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{7}$$

Where, K_{ads} is equilibrium constant of the adsorption process and C is inhibitor concentration. Linear plot obtained from Figure-3 shows that constituents of *o*-phenylenediamine on a brass surface making a barrier for charge and mass transfer between the metal and environment follows Langmuir adsorption isotherm which shows inhibition efficiency.

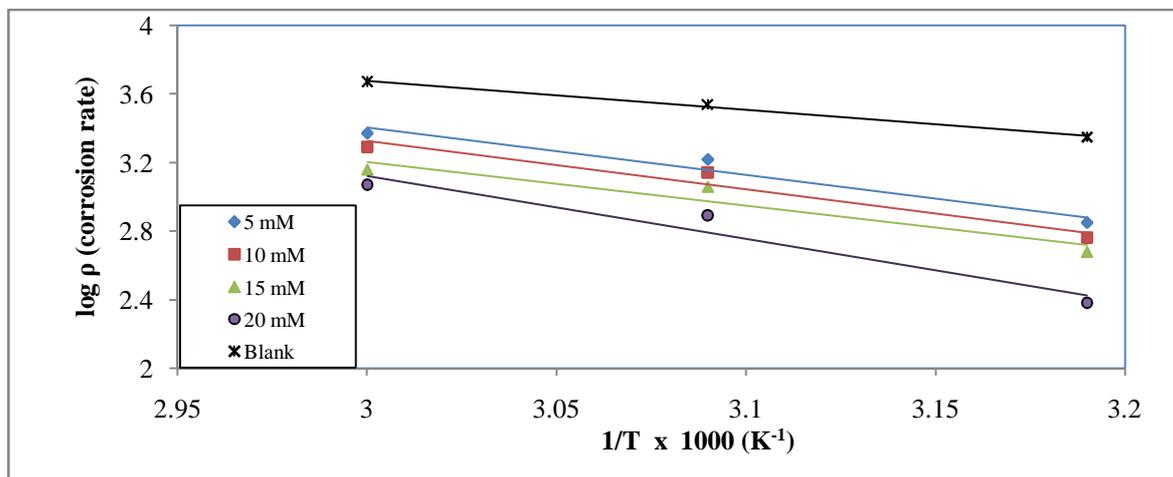


Fig. 2 : Arrhenius plots for brass in 0.1 M HNO₃ in absence and presence of the different concentration of *o*-phenylenediamine.

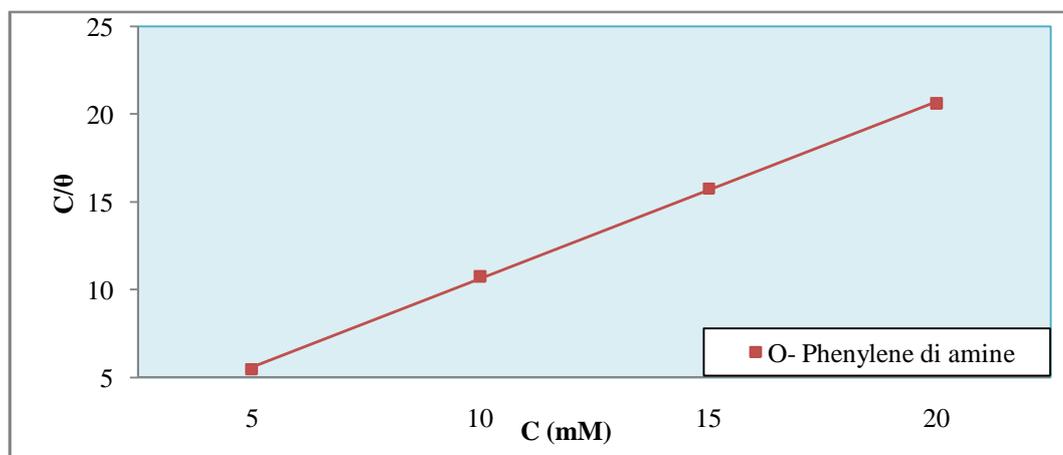


Fig. 3: Langmuir adsorption isotherm plot of C/θ versus ' C ' for brass in 0.1 M HNO₃ containing *o*-phenylenediamine as organic inhibitor at 301 K.

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3.4. Free energy determination

According to Eq. (7), K_{ads} can be calculated from intercept line on C/θ axis. This value of K_{ads} is also related to the standard free energy of adsorption ΔG_a° , as given by following equation [28,29]:

$$\Delta G_{ads}^\circ = -RT \ln (55.5 K_{ads}) \quad (8)$$

Where, R is the gas constant, T is the absolute temperature (K) and the value 55.5 in the above equation is the concentration of water in solution in Molar [30], K_{ads} is the equilibrium constant of the adsorption/desorption process. Calculated values of ΔG_a° are negative indicating that the adsorption process occurs spontaneously. The obtained values are close to -7.0 kJmol^{-1} , these reflect electrostatic interaction between the inhibitor and positively charged metal surface and may be described by physical adsorption [31]. The values of ΔG_a° decreases (become less negative) with increasing temperature. Therefore, it is evident from this trend that the strength of adsorption and hence I.E. decreases with rising temperature. This is concluded on the fact that the values of $\Delta G_{ads}^\circ -20 \text{ kJmol}^{-1}$ are consistent with physisorption, while those around -40 kJmol^{-1} or higher are associated with chemisorption [32]. The enthalpy of adsorption (ΔH_a°) and entropy of adsorption (ΔS_a°) are calculated using the equations (9) and (10).[33].

$$\Delta H_a^\circ = E_a - RT \quad (9)$$

$$\Delta S_a^\circ = \Delta H_a^\circ - \Delta G_a^\circ / T \quad (10)$$

The results revealed that ΔH_a° values are 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 brass corrosion reaction. The enthalpy change ΔH_a° was positive and ranging between 28.21 to 94.86 kJmol^{-1} indicating the endothermic nature of the reaction suggests that higher temperature favors the corrosion process. Positive value of ΔS_a° lie between 0.18 to $0.36 \text{ kJmol}^{-1} \text{ K}^{-1}$ indicate the affinity of the adsorbent for the inhibitor and the corrosion process is entropically favorable.

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

As concentration of inhibitor increases rate constant 'k' decreases whereas the half-life values are increases with increasing concentration of inhibitor. The increase in Half-life indicates more protection of the metals by OPD. The results are in good agreement with the result obtain by Ebenso [34] and Muthukumar and Chandrasekaran [35]. Corrosion rate constant 'k' increases with increases in concentration of acid (Table 4). From the rate constant values, the half-life values, $t_{1/2}$ of the metal in test solutions are calculated using the equation:

$$t_{1/2} = 0.693 / k \quad (11)$$

Table 4 : Kinetic data for the corrosion of brass in various concentration of HNO_3 containing Orthophenylenediamine.

Inhibitor	Inhibitor concentration (mM)	Acid concentration							
		0.1 M		0.25 M		0.5 M		1.0 M	
		Rate const. ($\text{k} \times 10^{-3}$)	Half life ($t_{1/2}$)	Rate const. ($\text{k} \times 10^{-3}$)	Half life ($t_{1/2}$)	Rate const. ($\text{k} \times 10^{-3}$)	Half life ($t_{1/2}$)	Rate const. ($\text{k} \times 10^{-3}$)	Half life ($t_{1/2}$)
Blank	---	29.41	23.56	108.34	6.40	160.68	4.31	295.28	2.35
Ortho Phenylene diamine	5	2.63	263.50	9.73	71.22	57.18	12.12	148.30	4.67
	10	1.97	351.78	8.41	82.40	43.39	15.97	113.27	6.12
	15	1.54	450.00	6.57	105.47	35.61	19.46	89.53	7.74
	20	0.77	900.00	3.41	203.22	30.57	22.67	80.45	8.61

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3.6. Potentiodynamic polarization study

Figure-4 represents the potentiodynamic polarization curves of brass in 0.1 M HNO₃ in absence and presence of *o*-phenylenediamine. 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.) are given in Table-5. It was observed that the addition of *o*-phenylenediamine in acid solution indicates the significant decrease in corrosion current density (i_{corr}) and decrease in the corrosion rate with respect to blank (Table-5). There is significant change in the anodic and cathodic slopes after the addition of the inhibitor. There is significant change in the anodic and cathodic slopes after the addition of the inhibitor and slightly shifted towards cathodic region. The value of E_{corr} is -0.045 V in uninhibited acid while it is shifted to the anodic side (-0.05 V) for inhibited acid. Tafel curves shows in Figure 4 that inhibitor is a mixed type of an inhibitor. In general, an inhibitor is anodic or a cathodic if the variation E_{corr} against the blank is higher or above 85 mV [36,37]. In this study, the displacement of E_{corr} was 5 mV which is less than a 85 mV (Table 5), which suggest that the OPD function as a mixed-type of inhibitor.

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

$$I.E. (\%) = \frac{i_{corr}(uninh) - i_{corr}(inh)}{i_{corr}(uninh)} \quad (12)$$

Table -5: Potentiodynamic polarization data and Inhibition efficiency (I.E.) of OPD as organic inhibitor for brass in 0.1 M HNO₃.

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)	Polarization method	Weight loss method
Blank	-0.045	1408	6.734	2.986	0.899	-	-
<i>o</i> -phenylene diamine	-0.050	113.90	12.198	4.327	1.389	91.91	97.41

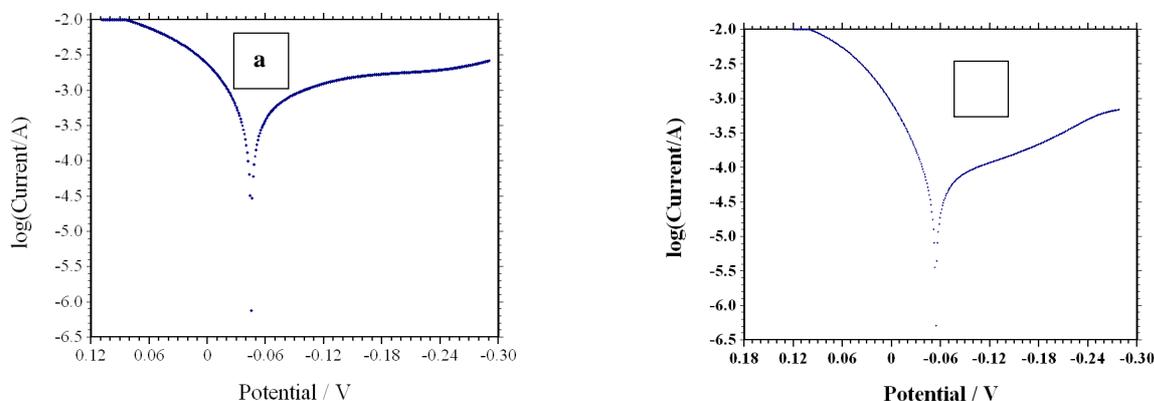


Fig.4: Potentiodynamic polarization curves for brass (a) in 0.1 M HNO₃ and (b) in 0.1 M HNO₃ in presence of 20 mM *o*-phenylenediamine.

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3.7. Electrochemical impedance spectroscopy (EIS) measurements

Nyquist plots for the corrosion of brass in 0.1 M HNO₃ solution in absence and presence of OPD was examined by EIS method at room temperature was shown in Table-6 and in Figure-5. It is observed from Figure-5 that the impedance diagram is almost semi circular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion [39]. The semi circular nature of the plots indicates that the corrosion of brass is mainly controlled by charge transfer process [40]. 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 [41].

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{13}$$

Where ‘f’ is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [42].

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

$$I.E. (\%) = \frac{C_{dl}(uninhi.) - C_{dl}(inhi.)}{C_{dl}(uninhi.)} \times 100 \tag{14}$$

The addition of inhibitor increase R_{ct} value from 320 (blank) to 2416.69 Ω cm² at the same time C_{dl} value decrease from 4.327 (blank) to 0.1428 μF/cm² which is due to the adsorption of inhibitor on the metal surface [Table-6]. 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. The decrease in the value of C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [43]. The changes in C_{dl} values can be a sign that there is gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface. Thus, it decreases the extent of metal dissolution [44].

Table –6: EIS parameters for corrosion of Brass in 0.1 M HNO₃ containing orthophenylenediamine.

System	R _{ct} (Ω cm ²)	C _{dl} (μF / cm ²)	IE(%) Calculated from	
			EIS method	Weight loss method
Blank	320.00	4.327	-	-
<i>o</i> -phenylenediamine	2416.69	0.1428	96.69	97.41

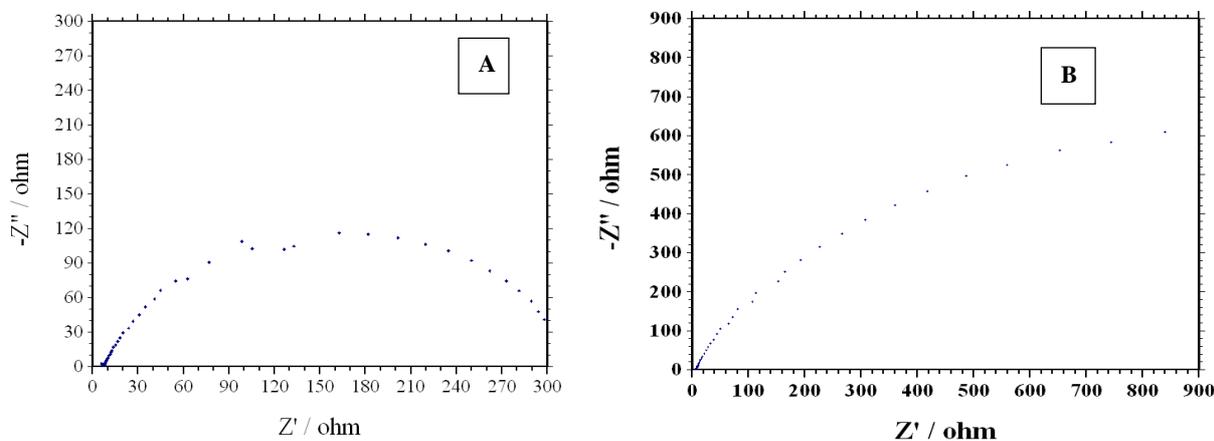


Fig.-5: Nyquist plot for brass in (A) in 0.1 M HNO₃ (Blank) (B) in 0.1 M HNO₃ in presence of 20mM *o*-phenylenediamine.

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3.8. Scanning Electron Microscopy (SEM) study

The SEM images of the brass surfaces exposed to 0.1 M HNO₃ in absence and presence of 20 mM of inhibitor for 24 h are presented in Fig. 6a–c. The Fig. 6 (a), shows micrograph of the polished brass plate shows smooth surface of the metal. The SEM micrographs (X 1000) of brass surface immersed in 0.1 M HNO₃ in Fig. 6b shows roughness of the metal surface which indicates the corrosion of Brass. The corrosion products appear very uneven and lepidoteral-like morphology. Fig.6(c) showed the SEM image of the brass surface exposed in inhibited acid (0.1 M HNO₃ + 20 mM inhibitor). The metal surface is almost free from corrosion due to the formation of insoluble complex on the surface of metal. In the presence of inhibitor, the surface is covered by a thin layer of inhibitor which effectively controls the dissolution of brass.

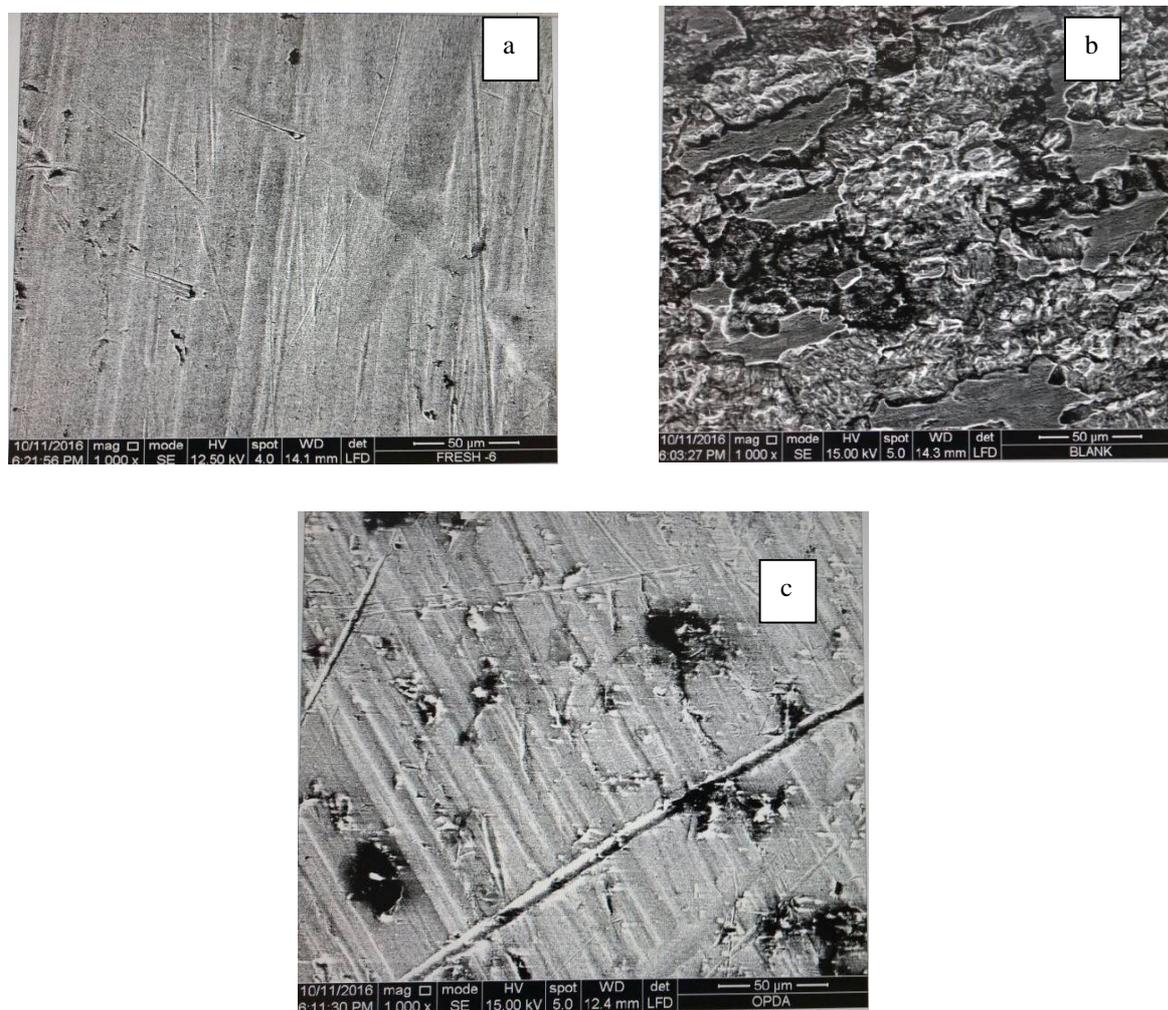


Fig.-6: SEM micrographs of brass surface (a) before immersion (Polished) (1000 X), (b) after immersion in 0.1 M HNO₃ in absence of inhibitor (1000 X), (c) after 24 h immersion in 0.1 M HNO₃ in presence of 20 mM OPD at 301 K (1000 X).

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3.9. Mechanism of corrosion

The behaviour of anodic dissolution of brass in nitric acid is very complex and consists of dissolution of both zinc and copper. Generally, the anodic reaction for Cu is considered as follows [45-47]:



Where $\text{Cu (I)}_{\text{ads}}$ is an adsorbed species onto copper surface and does not diffuse into the bulk solution. Meanwhile, the adsorption of copper ions, Cu (II) , on the surface due to its reduction in presence of Zn must be taken into consideration. Also, the anodic dissolution of Zn is considered according to following equation:



It should be noticed that the cathodic reaction is not hydrogen evolution reaction at all, because the corrosion potential in all experiments is well above the redox potential of hydrogen evolution in this media. In this way, the predominant mechanism of cathodic reaction has been reported according to the following equation [48]:



Also, oxygen reduction in acidic media can be considered to be as another cathodic reaction. Based on Eq.(18), the presence of NO_3^- ions onto cathodic sites is mandatory for reaction.

4.0. Mechanism of inhibition

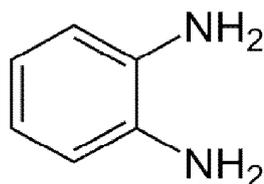


Fig.-7 : Structure of orthophenylenediamine ($\text{C}_6\text{H}_8\text{N}_2$)

Inhibition of corrosion can be attributed to the strong adsorption of the compound on the metal surface by the electron transfer from the organic molecule to the metal surface to form a coordinate type of link. As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitors at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Inhibition of corrosion of brass in HNO_3 solution by the inhibitors can be explained on the basis of adsorption. Four types of adsorption may take place involving organic molecules at the metal-solution interface: (i) Electrostatic attraction between charged molecules and the charged metal, (ii) Interaction of unshared electron pairs in the molecule with the metal, (iii) Interaction of π -electrons with the metal and (iv) Combination of all the above. It is apparent that the adsorption of these organic inhibitors on the metal surface could occur directly on the basis of donor acceptor interaction. Moreover, the presence of inhibitors in the organic structures makes the formation of $d\pi$ - $d\pi$ bond which enhances the adsorption of the compounds on the metal surface. These compounds inhibit the corrosion by controlling both the anodic and cathodic reactions. In an acidic solution, these compounds can exist as protonated species. These protonated species may adsorb on the cathodic sites of brass surface and decrease the evolution of hydrogen. The adsorption of these compounds on anodic sites may decrease anodic dissolution of brass. The formation of positively charged species in an acidic medium also facilitates the adsorption of the compound on the metal surface through electrostatic interactions between the organic molecule and the metal surface. The availability of an electron in the benzene ring in OPD and nitrogen plays a

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vital role in the inhibitor to the brass surface. Thenitrogen atoms present in OPD enhance the efficiency [18]. In aqueous acidic solutions amines exist as neutral molecules, involving the displacement of water molecules from the metal surface and sharing of electrons between the nitrogen atom and the metal surface. It has already been observed that the extent of adsorption of the amine is influenced by the nature of anions in acidic solutions. [9].

IV. CONCLUSIONS

1. Corrosion rate increases with increase in acid concentration and with temperature.
2. As the inhibitor concentration increases corrosion rate decreases while I.E. increases.
3. Orthophenylenediamineadsorbed on metal surface follows Langmuir adsorption isotherm.
4. Maximum I.E. was found 97 % in 0.1M HNO₃with 20 mM inhibitor concentration.
5. Tafel plot of polarization measurements indicates that the inhibitor behave as a mix type inhibitor.
6. EIS spectra exhibit semicircular in appearance which indicates that the corrosion of brass is mainly controlled by charge transfer process.
7. The SEM images confirm the formation of protective layer on the metal surface.

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