Electrochemical Experimental Studies on Inhibition Efficiency of Substitued Piperidin-4-One on the Corrosion of Copper in Nitric Acid Media

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Abstract: The inhibition efficiency of 2,6-diaryl-3-methyl-piperidin-4-one (3MNH) on the corrosion of copper was studies in 1.0M HNO_3 solution by potentiodynamic polarization techniques and electrochemical impedance spectroscopy in the nitric acid media, a mixed type of inhibition mechanism was observed by 3MNH, but with dominant cathodic nature. Langmuir adsorption isotherm was found to fit well with the experimental data. The adsorption of 3MNH onto copper surface is of both physisorption and chemisorption which is proved by the thermodynamic parameters such as adsorption equilibrium constant (K_{ads}), free energy of adsorption (ΔG_{ads}), activation energy (E_a) and potential of zero charge (pzc).

Key words: Copper; piperidin-4-one; electrochemical impedance spectroscopy; potentiodynamic polarization; pzc.

1. Introduction

Copper is a metal widely used for its electrical and thermal conductivities in many industrial applications such as fabrication of alloys of copper, manufacture of industrial equipment, building construction materials, electrical, ornamental parts, electronics and coinages, etc.,[1-3]. Corrosion of copper in acidic and strongly alkaline media have been the topics of interest for researchers for quite some time now. Corrosion of copper in non-oxidizing acidic environment is not possible, since hydrogen evolution is not a part of a corrosion reaction. In the presence of oxygen and oxidizing agents like Fe^{3+} and NO_3^- copper corrodes more because the copper oxides are soluble in acidic pH[4-5]. Corrosion of copper in nitric acid is one of the most widely studies research area[6,7]. About 25-30% of annual corrosion cost could be saved with the help of suitable corrosion management practices[8]. Usage of organic molecules inhibitor is one of the most practical methods for protection against corrosion in acidic media[9,10]. The inhibitor molecule and the metal surface are interacted by means of physisorption or chemicsorption or by both[8-11].

In the present work 3MNH was synthesized and used the same as corrosion inhibitor for copper in 1.0M HNO_3 acid media. The inhibition of corrosion was studied by potentiodynamic polarization studies and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1 Materials and methods

A teflon coated cylindrical copper electrode with an exposed area of $0.2826cm^2$ having a composition of 99.5% Cu, 0.003%Ni, 0.019%Al, 0.002%Mn and 0.116%Si was used for polarization and electrochemical impedance studies. The surface was polished using emery papers of various grades in the following order (1/0, 2/0, 3/0. 4/0 and 5/0), degreased with acetone and dried with nitrogen, prior to the electrochemical studies. All experiments were carried out at room temperature (28±1°C). All chemical were purchased from Sigma Aldrich and E Merck and used without further purification, laboratory double-distilled water was used for all studies. Stock solution of inhibitor was prepared in 2.5M solution of nitric acid.

2.2. Synthesis of 2,6-diaryl-3-methyl-piperidin-4-one

The inhibitor was prepared by the following procedure of Mannich reaction[12].
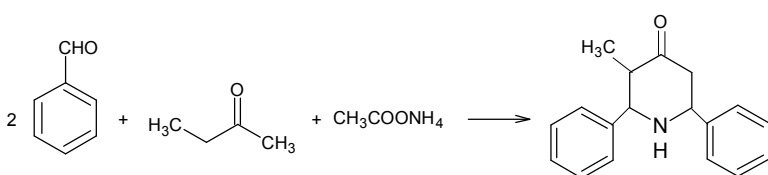
A mixture of ethyl methyl ketone (0.1mole), dried ammonium acetate (0.1mole), benzaldehyde (0.2mole) are added in 30mL of ethanol and heated to simmering carefully. It was kept at room temperature for 12 hours. Dry ether (50mL) was added followed by concentrated hydrochloric acid (30mL) are added under ice cold condition. The precipitated hydrochloride was filtered and washed repeatedly with a 1:5 mixture of ethanol and ether. The hydrochloride was suspended in acetone, and made alkaline using ammonia solution. On dilution with excess of water, the base was precipitated which was filter, vacuum dried and recrystallized from absolute alcohol[13]. The structure of 3MNH is shown in Fig.1.
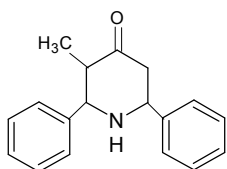

Figure 1: Structure of 2,6-diaryl-3-methyl-piperidin-4-one (3MNH)

2.3. Electrochemical impedance studies

A three electrode set up was used for the electrochemical studies, in which a saturated calomel electrode (SCE), a Pt foil and teflon coated copper rod were used as reference, counter and working electrode respectively. Stabilizatyion period of 45 minutes was allowed to attain a stable E_{ocp}Vs (SCE) before the electrochemical impedance studies are carried out. EIS measurements were done using a GAMRY reference 600 potentiostat and the data were analyzed using GamryEchem analyst software. The AC frequency range was between 100kHz to 10mHz with an external perturbation of 10mV. A nonlinear least square fitting adopted for processing the data[14]. Inhibition efficiency (IE%) was calculated by the following equation.

$$IE\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} X 100$$

Where R'_{ct} and R_{ct} are the charge transfer resistance values in the inhibited and uninhibited solutions respectively.

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2.4. Potentiodynamic polarization measurements

The same three electrode setup used in electrochemical impedance study was used to measure the potentiodynamic polarization curves. The potential is swept at the rate of 1.6mVs^{-1}, from the negative potential OCP to the positive potential of OCP through corrosion potential[15]. The inhibition efficiencies were calculated using the relationship[16].

$$IE\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100$$

Where i_{corr} and i'_{corr} are the corrosion current densities without and with inhibitor respectively.

2.5. Measurement of the potential of zero charge (pzc)

Potential of zero charge is the electrode potential at which a metal/solution interface displaya a net zero charge on the bare metal (oxide-free) surface. By applying different applied DC potential at the AC frequency of 20kHz, the electrochemical impedance spectra were recorded. A graph is plotted between the double layer capacitance values and the applied potential, from which the potential of zero charge is calculated[17].

2.6. Determination of activation energy

The effect of temperature on the inhibition efficiency for copper in 1.0M HNO$_3$ in the absence and presence of different concentratiosn of inhibitor at different temperature ranging from 35°C to 55°C was obtained by carrying out the potentiodynamic polarization studies[18]. Arrhenius equation is used to measure the change of corrosion rate with respect to temperature[17,18].

$$i_{corr} = Ae^{-\frac{E_a}{RT}}$$

Where i_{corr} is the corrosion current density, A is the Arrhenius pre-exponential constant, R is the universal gas constant, E$_a$ is the energy of activation and T is the absolute temperature.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

The impedance spectra were recorded at 28±1°C in the presence and in the absence of inhibitor in 1.0M HNO$_3$ solution is shown in Fig.2. The size and the shape of the impedance spectra changes due to the presence of inhibitor. It can be noted that the impedance psectra showed a depressed semicircle loop at higher frequencies, which may be due to the surface heterogeneity caused by the micropscopic surface roughness of electrode surface and the inhibitor adsorption[19,20]. The presence of Warburg impedance could be attributed to oxygen transport from the bulk solution to the metal surface[15]. From the impedance spectra it is clear that the size of the semicircle increases with the increase in concentration of 3MNH. This is a clear indication that the 3MNH increases the charge transfer resistance and had an inhibiting effect on the corrosion of copper in 1.0M HNO$_3$[21,22]. The decrease of Warburg impedance on the higher concentrations of inhibitor is an indication of more adsorption of inhibitor molecule on the copper surface, which prevents the diffusion of oxygen into the solution-metal interface[23]. The experimental curves fit well with the equivalent circuit shown in Fig.3. Constant phase element (CPE) is most often used to represent the non-ideal capacitive behavior, which has the impedance function in the following form[21-23].

$$Z_{cpe} = \frac{1}{Y_0 (j\omega)^n}$$

Where Y$_0$ is the admittance of the corrosive system at 1rad s^{-1} and n is a constant ($-1 \leq n \leq 1$) when n=0, the CPE represents pure resistor, if n=+1 CPE represents pure capacitor and if n=-1 it represents an inductor[24]. Highly polished and clean metal surface will have the value of n near unity[25]. From the table 1 the values of n for the corroding copper electrode in the 1.0M HNO$_3$ media is near by 1. The surface heterogeneity decreased

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with increase in inhibitor concentration, which results in the higher value of n for higher concentration of 3MNH in 1.0M HNO_3. The idealized capacitance value (c_{id}) is calculated from the CPE parameters using the following expression[22-24].

$$\sin\left(n\left(\frac{\square}{2}\right)\right))$$

Where 'ω'' is the angular frequency at the maximum value of the imaginary part of impedance $-Z$''.

It is further seen that this value of angular frequency is calculated using the expression[23].

$$C_{dl} = Y_0(()^{n-1}$$

Table 1 Electrochemical parameters for copper in 1.0M HNO_3 solution in the presence and absence of inhibitor from EIS.

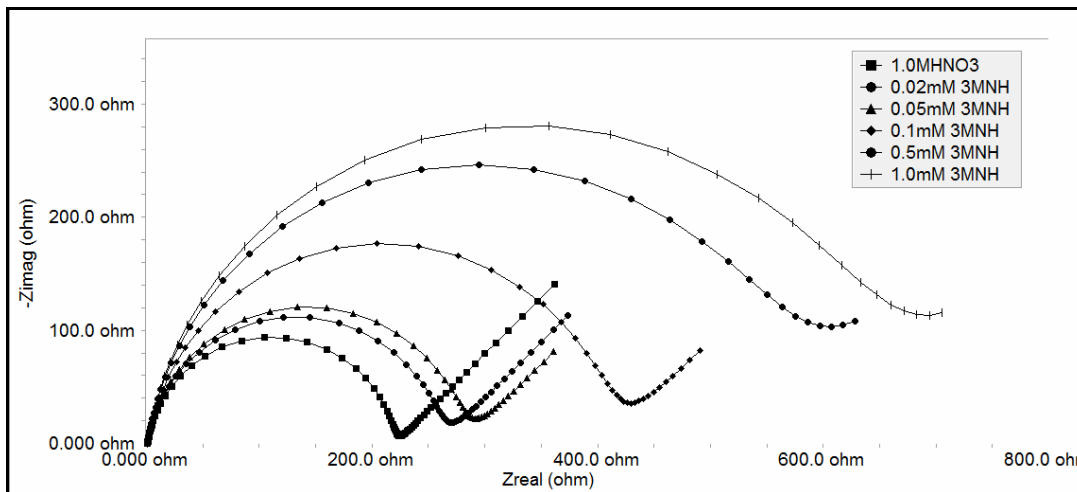| Medium	Inhibitor Concentration (mM)	R_{ct} Ωcm^2	Y_0 (X 10^{-6}) $\Omega^{-1}cm^{-2}$	n	C_{dl} μFcm^{-2}	Inhibitor efficiency (IE%)
	Blank	204	943	0.914	196	-
	0.02	272	687	0.854	113	25
1.0M	0.05	297	328	0.869	109	31
HNO_3	0.10	431	186	0.912	97	53
	0.50	602	115	0.918	62	66
	1.0	687	64	0.897	49	71

Figure 2. The Nyquist plots for Cu electrode obtained in 1.0M HNO_3 in the absence and in the presence of 3MNH at various concentrations.
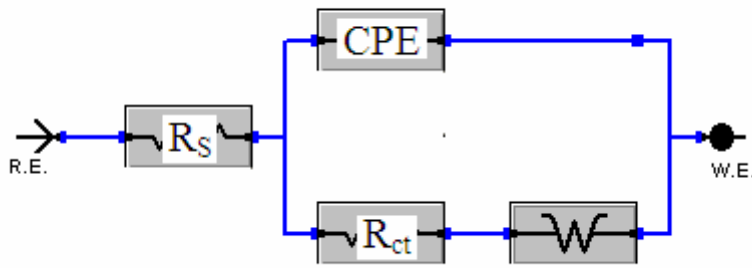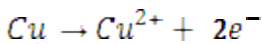
Figure 3. Equivalent circuit for the Cu surface/corrosive media interface with CPE in acid media.

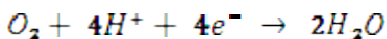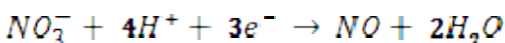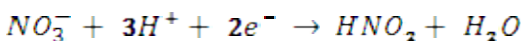### 3.2. Potentiodynamic polarization measurements

Fig.4 present the potentiodynamic polarization curves of copper in 1.0M HNO_3 solution with and without 3MNH. Earlier studies confirmed that the dissolution of copper in the naturally aerated acidic medium follows the mechanism discussed below[26].

Copper corrodes to Cu^{2+} in nitric acid and no passive oxide fillm is formed to protect the surface. Dissolution of copper is the dominant reaction in the HNO_3 media[26]. The electrochemical reaction is as follows[26,27]:

Anodic reaction:

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

Cathodic reaction:

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The polarization plots were analyzed by Tafel extrapolation method to calculate the corrosion kinetics parameters such as, corrosion potential (E_{corr}), corrosion current (i_{corr}), cathodic and anodic slopes and inhibitor efficiency were given in table 2. From the table it is clear that the addition of inhibitor decreasing the corrosion rate with increase in the concentration of 3MNH in 1.0M HNO_3 medium. Since, the shift of E_{corr} after the addition of inhibitor was found to be less than 80mV in the present study, the mechanism of inhibition of 3MNH on 1.0M HNO_3 can be considered as mixed type[28]. Change in value of cathodictafel slope (β_c) with increase in inhibitor concentration indicates that the proton reduction reaction was affected by the addition of inhibitor. Change in value of anodic tafel slope (β_a) with increase in inhibitor concentration indicates that the inhibitor was first absorbed on the metal surface and blocked the reaction sites of metal surface[29].
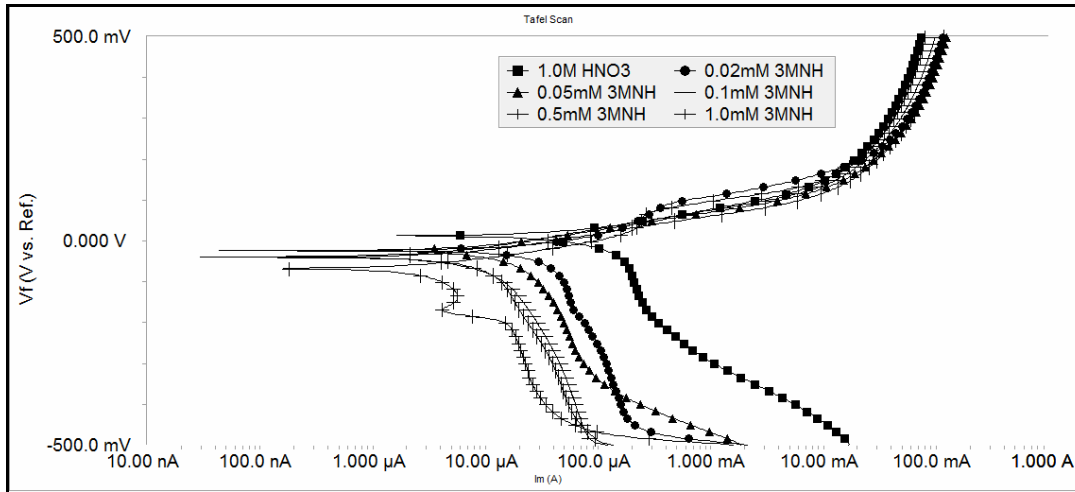
Figure 4. Tafel plots for Cu in 1.0M HNO₃solution in the absence and inthe presence of 3MNH at various concentrations.

Table 2 Electrochemical parameters for copper in 1.0M HNO₃ solution in the presence and absence of inhibitor from Tafel polarization curves.

Medium	Inhibitor Concentration (mM)	E_{corr} (mV)	I_{corr} (mA)	β_c (mV dec^{-1})	β_a (mV dec^{-1})	Inhibitor efficiency (IE %)
	Blank	12.8	0.099	377	62.9	-
	0.02	-22.6	0.069	374	117.7	30.3
1N HNO₃	0.05	-23.4	0.052	362	50.2	47.5
	0.10	-38.5	0.047	207	51.8	52.5
	0.50	-39.9	0.032	217	48.7	67.7
	1.0	-67.6	0.024	215	79.6	75.8

3.3. Adsorption isotherm

The surface coverage degree (Θ) at different temperatures (35°C, 45°C and 55°C) were calculated from the inhibition spectroscopy efficiency of 1.0mM 3MNH in 1.0M HNO₃ using the following relationship:

$$Surface\ coverage\ (\Theta) = \frac{Inhibition\ efficiency\ (IE)}{100}$$

Interaction among the adsorbed molecules and the interaction with the electrode surface can be understood by their adsorption behavior[30]. In the present study the Langmuir isotherm provides the best correlation with the experimental data and it is expressed as follows:

$$C_{inh}/\theta = C_{inh} + 1/K_{ads}$$

WhreC_{inh} is the concentration of the inhibitor, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant. The Langmuir isotherm plots are given in Fig.5, from the plot of C_{inh}vsC_{inh}/θ at constant temperature, the value of K_{ads}can be determinedstandard free energy of adsorption can be calculated using the following expression[31]:

$$K_{ads} = 1/55.5\ exp^{-\Delta G/RT}$$

The correlation coefficient of Langmuir isotherm plots are greater than 0.9 and were linear. At room temperature the value of $\Delta G_{ads}$is found to be -35.37kJmol^{-1}.for 1.0M HNO₃ which reveals that the spontaneous adsorption of the inhibitor molecule is possible onto the metal surface If the -ΔG_{ads}value is about 20kJmol^{-1}the

adsorption of inhibitor molecule on the metal surface will be of physisorption and if the value is greater than 40kJmol^{-1}then the adsorption will be due to chemisorption. If the value of -ΔG_{ads} lies between 20kJmol^{-1} and 40kJmol^{-1}, it represents possibility of having both physisorption and chemisorption[32]. In the present study, the value of -$\Delta G_{ads}$is in between 20 and 40kJmol^{-1} the adsorption of inhibitor molecule follows both chemisorption and physisorption but more contribution from chemisorption[32]. Arrhenius plot for the 1.0M HNO$_3$ with and without inhibitor is shown in Fig.6. From the table 3 it is clear that the activation determined is less for the inhibited solution than that of the uninhibited solution which support the chemisorption of inhibitor molecule on the metal surface[33].
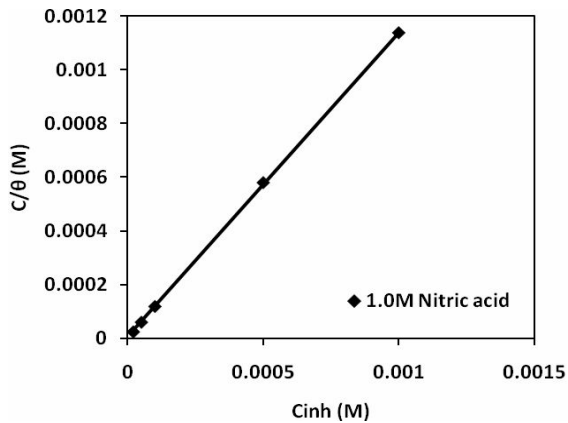

Figure 5. Langmuir Adsorption Isotherm for the adsorption of 3MNH on the coppermetal surface in 1.0M HNO$_3$ solution.
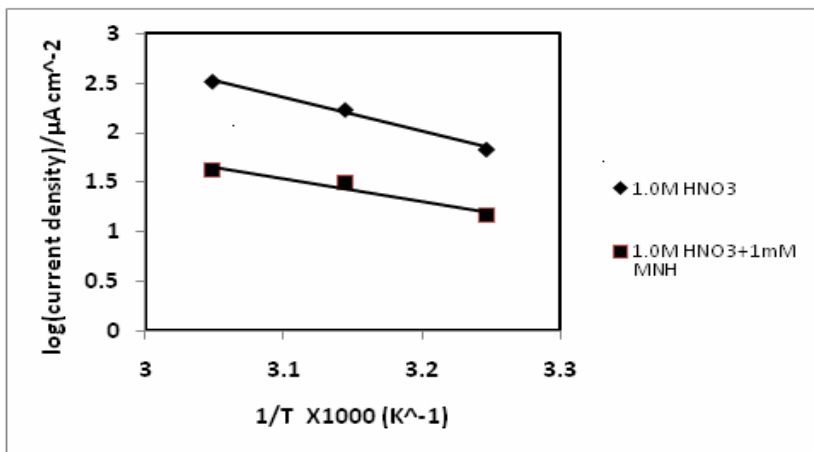

Figure 6. **Arrhenius plots for corrosion of Cu in 1.0M HNO$_3$solution in the absence and in the presence of 3MNH (1.0mM).**

Table.3 Thermodynamic parameters obtained from potentiodynamic polarization studies

Medium	$K_{ads(M^{-1})}$	$\Delta G_{ads(KJ/mol)}$	$E_{a(KJ/mol)}$	Linear regression coefficient(r)
1.0M HNO$_3$	-	-	73.21	0.927
1.0MHNO$_3$+Inhibitor	42,548	-38.47	57.92	0.951

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3.4. Potential of zero charge

Adsorption behavior of organic molecule onto the metal surface depends on structure of organic molecule, surface charge density and potential of zero charge (pzc)[34]. Fig.7 shows the graphical representation of dependence of double layer capacitance on the applied DC potential. The values open circuit potential (E_{ocp}) and pzc are given in table 4. The surface charge of copper at the open circuit potential was calculated using the equation $E_r = E_{ocp} - E_{pzc}$, where, E_r is Antropov's rational corrosion potential[34]. From the table 4 it is clearly understood the nitrate ions get adsorbed on the metal surface first, because the metal surface is positively charged with respect to pze in 1.0M HNO_3, the protonated inhibitor molecule forms a bond with the adsorbed nitrate molecule to prevent the metal dissolution[14].
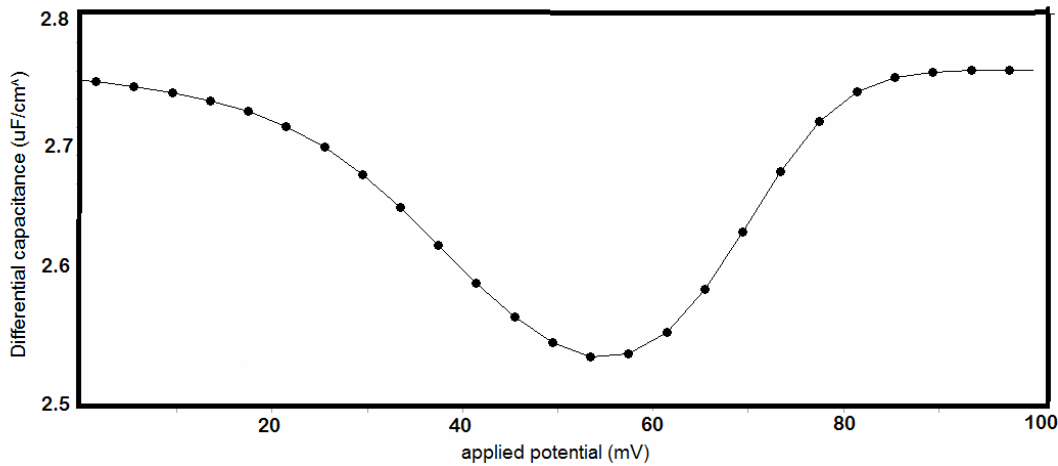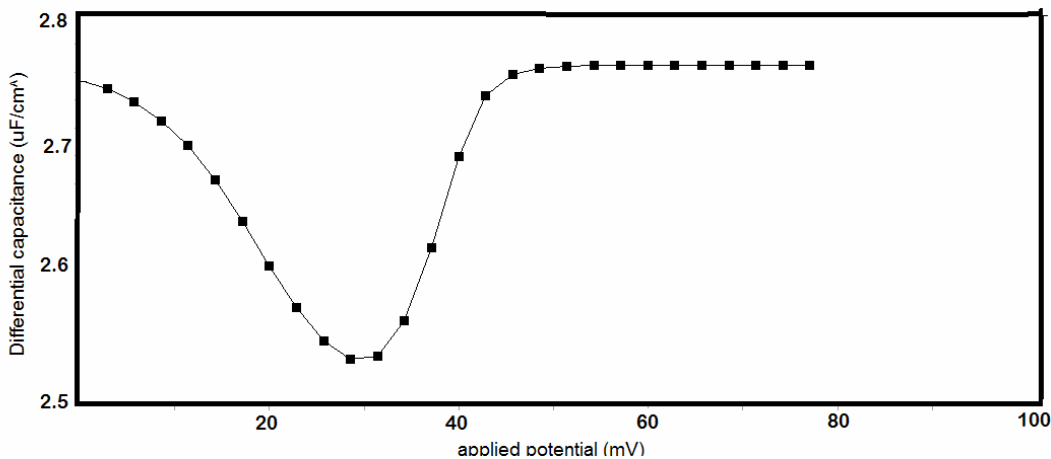

Fig. 7a

Fig. 7b

Figure 7.The plot of differential capacitance vs. applied electrode potential for copper in (a) 1.0M HNO_3 solution,(b) 1.0M HNO_3 containing 0.5mM 3MNH.

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Table.4 Excess charge on Cu electrode in 1.0M HNO₃ solution in the presence and absence of the inhibitor

Medium	E_{OCP}(mv/SCE)	PZC(mv/SCE)	Excess chargeE_{OCP}-E_{PZC}
1.0M HNO₃	+61.2	+58	+3.8
1.0MHNO₃+0.5mM of inhibitor	+33.0	+29	+5.0

4. Conclusion

From the present study, the following were the important conclusions, 3MNH is found to be safe corrosion inhibitor for copper in 1.0M nitric acid medium. The maximum inhibition efficiency was found be at 1.0mM dose of inhibitor. Potentiodynamicstuies have shown that the 3MNH act as mixed type inhibitor with dominant cathodic nature. The inhibition efficiency is related to the concentration of the inhibitor molecule. Langmuir adsorption isotherm fits well experimental results. The adsorption is found to be spontaneous and exothermic. The decrease in activation energy with the addition of inhibitor also confirms the more contribution of chemisorption.

Acknowledgement

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