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Electrochemical impedance spectroscopy and weight loss study for new pyridazine derivative as inhibitor for copper in nitric acid

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ABSTRACT

The inhibiting action of 5-[hydroxy(phenyl)methyl]-6-methylpyridazin-3(2H)-one (HPMP) on the corrosion of copper in nitric acid has been studied. The results from weight loss and electrochemical impedance measurements consistently identify HPMP as a good inhibitor. Impedance spectroscopy revealed that the corrosion of copper in nitric acid solution was influenced to some extent by charge transfer. The inhibition efficiency increases with increase in inhibitor concentration but decrease with rise in temperature (303-343K). The adsorption of HPMP onto the copper surface was found to follow the Langmuir adsorption isotherm. Various parameters (E_a, ΔG°_{ads}, K_{ads}) for adsorption reveal a strong interaction between inhibitor and copper surface. The negative values of ΔG°_{ads} indicate the spontaneous adsorption of the inhibitor on copper surface. Both kinetic parameters (activation energy, pre-exponential factor, enthalpy of activation and entropy of activation) were calculated and discussed.

Keywords*:* Copper; Nitric Acid; Corrosion Inhibition; Pyridazine; Weight Loss.

INTRODUCTION

Copper has been one of the preferred materials in industry owing to its excellent electrical and thermal conductivities, good mechanical workability, and relatively noble properties. It is commonly used as a material in heating and cooling systems. Scale and corrosion products have a negative effect on heat transfer, causing a decrease in heating efficiencies of the equipment, which is why periodic de-scaling and cleaning in nitric acid and hydrochloric acid pickling solutions are necessary. Corrosion inhibition of copper can be achieved through the modification of its interface by forming self assembled ordered ultrathin layers of organic inhibitors. Commonly used inhibitors for copper corrosion are toxic compounds that should be replaced with the new eco-friendly inhibitors. Most of the inhibitors are organic compounds and their derivatives such as azoles [1–20], pyridazine [21, 22], quinoxaline [23-26], amines [27], amino acids [28], thiophene and its derivatives [29-31] and many others. It is noticed that presence of heteroatoms such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the presence of vacant d orbitals in copper atom that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, π electrons, is also present. This paper reported our attempt to use electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, weight loss and theoretical calculations to investigate the nature of adsorption of Pyridazine on the copper surface. The structure of HPMP is shown in Fig. 1.

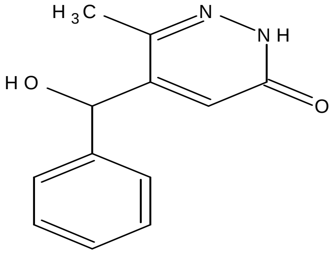

Fig .1 The molecular structure of HPMP.

MATERIALS AND METHODS

2.1. Materials and reagents

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities were used for electrochemical and gravimetric studies. The Copper samples were mechanically polished using different grades of emery paper, washed with double distilled water, and dried at room temperature. Appropriate concentration of aggressive solutions used (2M HNO_3) was prepared using double distilled water.

2.2. Electrochemical measurements

❖ Electrochemical cell

The electrolysis cell was a pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was copper with the surface area of 0.28 cm^2. Before each experiment, the electrode was polished using emery paper until 2000 grade. After this, the electrode was cleaned ultrasonically with distillate water. A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2.

The aggressive medium used here is 2M HNO_3 solution was prepared with concentrated HNO_3 and distilled water. The molecule structure of pyridazine tested are shown in Fig. 1. The concentration range of this compound was 10^{-6} to 10^{-3} M.

❖ EIS measurements

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (Tacussel Radiometer PGZ 301), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 303 K and an air atmosphere. The polarization resistance R_p, is obtained from the diameter of the semicircle in Nyquist representation.

2.3. Weight loss measurements

Gravimetric experiments were carried out in a double walled glass cell. The solution volume was 50 cm^3; the temperature of 303 K was controlled thermostatically. The weight loss of copper in 2M HNO_3 with and without the addition of inhibitor was determined after immersion in acid for 1 h. The copper specimens were rectangular in the form (2 cm ×2 cm × 0.20 cm).

RESULTS AND DISCUSSION

3.1.Gravimetric measurements

3.1.1. Effect of temperature and thermodynamic activation parameters

In order to study the effect of temperature on the inhibition efficiencies of HPMP, weight loss measurements were carried out in the temperature range 303–343K in absence and presence of inhibitor at optimum concentration. The corresponding data are shown in Table 1.

The corrosion rate (W) was calculated from the following equation:

$$W = \frac{(m_1 - m_2)}{(S.t)} \tag{1}$$

where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, S the total area of the specimen, t the corrosion time and W the corrosion rate.

With the calculated corrosion rate, the inhibition efficiency of inhibitor for the corrosion of C38 steel was obtained by using the following equation [32]:

$$IE_w(\%) = (1 - \frac{W_{corr}}{W^{\circ}_{corr}}) \times 100 \tag{2}$$

W_{corr} and W°_{corr} are the corrosion rate of steel samples with and without the inhibitor, respectively. The degree of surface coverage (□) was calculated using equation 3 [32]:

$$\Theta = 1 - \frac{W_{corr}}{W^{\circ}_{corr}} \tag{3}$$

Table 1. Various corrosion parameters for copper in 2M HNO_3 in absence and presence of optimum concentration of HPMP at different temperatures at 1h

Temperature (K)	Inhibitor	W($mg/cm^2.h$)	E_w (%)	Θ
303	Blank	1.78	-	-
	HPMP	0.12	93.2	0.932
313	Blank	7.33	-	-
	HPMP	0.50	93.2	0.932
323	Blank	24.97	-	-
	HPMP	3.41	86.4	0.864
333	Blank	70.82	-	-
	HPMP	17.97	74.6	0.746
343	Blank	186.61	-	-
	HPMP	76.35	59.1	0.591

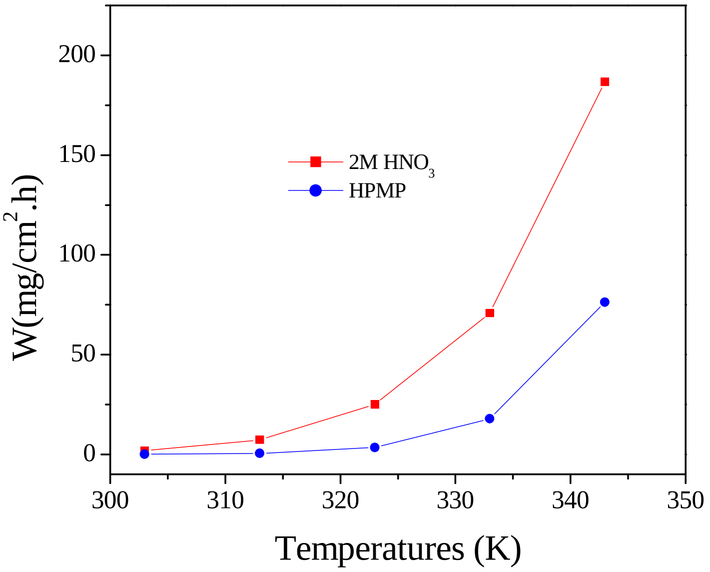

Fig 2. Variation of corrosion rate in 2M HNO_3 on copper surface without and with of optimum concentration of pyridazine at different temperatures

Inspection of Table 1 showed that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of HPMP decreased with temperature. A decrease in inhibition efficiencies with the increase temperature in presence of HPMP might be due to weakening of physical adsorption.

In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (4) and transition state Eq. (5) were used [33]:

$$C_R = A\exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^\circ}{R}\right)\exp\left(-\frac{\Delta H_a^\circ}{RT}\right) \tag{5}$$

Where C_R is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogrado's number, E_a the activation energy for corrosion process , ΔH_a° the enthalpy of activation and ΔS_a° the entropy of activation.

The apparent activation energie (E_a) at optimum concentration of HPMP was determined by linear regression between Ln C_R and 1/T (Fig. 3) and the result is shown in Table 2. The linear regression coefficient was close to 1, indicating that the copper corrosion in nitric acid can be elucidated using the kinetic model. Inspection of Table 2 showed that the value of E_a determined in 2M HNO_3 containing HPMP is higher (142.44 kJ mol^{-1}) than that for uninhibited solution (100.21 kJ mol^{-1}). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [34]. Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the copper surface with increase in temperature. As adsorption decreases more desorption of inhibitor molecules occurs because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of copper comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature [35].

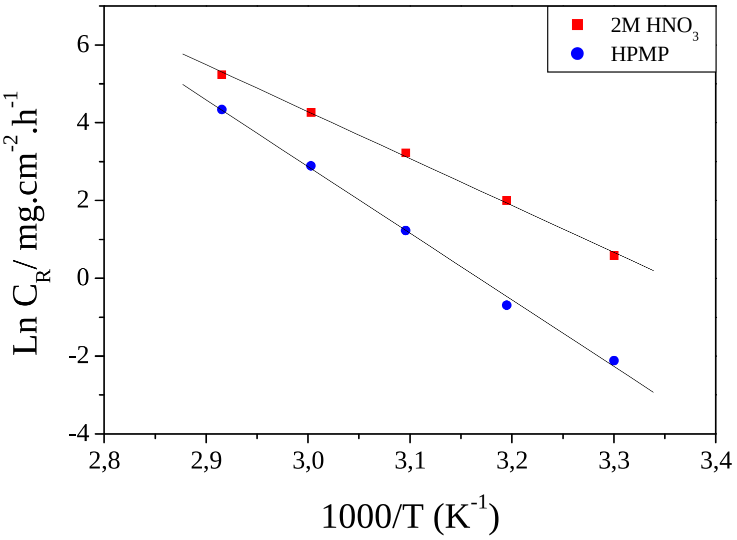

Fig. 3. Arrhenius plots of log C_R vs. 1/T for copper in 2M HNO_3 in the absence and the presence of HPMP at optimum concentration.

Fig. 4 showed a plot of Ln (C_R/T) versus 1/T. The straight lines are obtained with a slope (ΔH°_{a} /R) and an intercept of (Ln R/Nh + $\Delta S°_a$ /R) from which the values of the values of ΔH°_{a} and ΔS°_{a} are calculated and are given in Table 2. Inspection of these data revealed that the thermodynamic parameters (ΔH°_{a} and ΔS°_{a}) for dissolution reaction of copper in 2M HNO_3 in the presence of HPMP is higher (139.76 kJ mol^{-1}) than that of in the absence of inhibitors (97.53 kJ mol^{-1}). The positive sign of ΔH°_{a} reflect the endothermic nature of the copper dissolution process suggesting that the dissolution of copper is slow [36] in the presence of inhibitor.

Table 2 Activation parameters for the copper dissolution in 2M HNO_3 in the absence and the presence of HPMP at optimum concentration

	A (mg/cm^2.h)	Linear regression coefficient (r)	E_a (kJ/mol)	ΔH°_{a} (kJ/mol)	ΔS°_{a} (J/mol.K)	K_{ads} (M^{-1})	ΔG°_{ads} (kJ/mol)
Blank	3.6627×10^{17}	0.99908	100.21	097.53	082.36	-	-
HPMP	3,7074×10^{23}	0.99852	142.44	139.76	197.32	147761.1	-40.10

The entropy of activation ΔS°_{a} in the absence of inhibitor is positive and this value increases positively with the HPMP. The increase of ΔS°_{a} implies that an increase in disordering takes place on going from reactants to the activated complex [37].

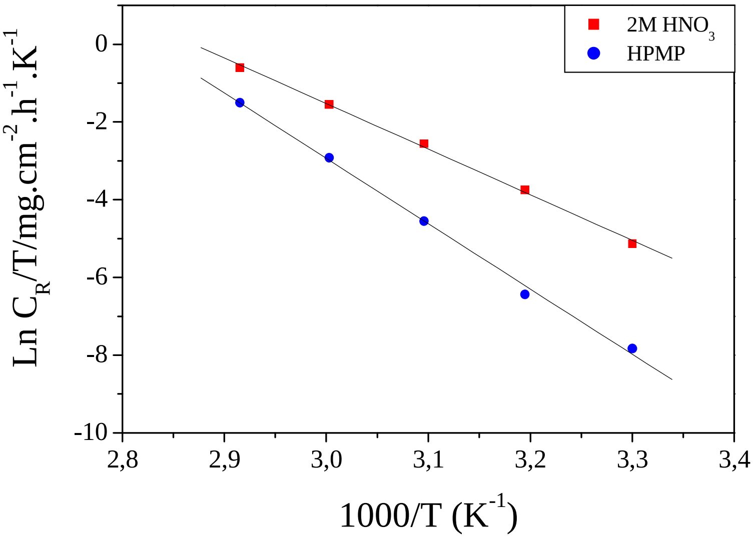

Fig. 4. Arrhenius plots of log C_R/T vs. 1/T for copper in 2M HNO_3 in the absence and the presence of HPMP at optimum concentration.

3.1.2. Adsorption isotherm

Basic information on the interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm, and the type of the inhibitors on metal is influenced by (i) the nature and charge of the metal (ii) chemical structure of the inhibitor and (iii) the type of electrolyte. The degree of surface coverage (Θ) of copper electrode by adsorption of investigated compounds was calculated using the equation 3.

The values of (Θ) for different concentrations of the studied compounds at 303K have been used to explain the best isotherm to determine the adsorption process. The adsorption of this compound, on the surface of copper is regarded as a substitution adsorption process between organic compound in aqueous phase [Org(sol)] and the water molecules adsorbed on Cu surface [H_2O(ads)] [38]:

$$\mathrm{Org}_{(sol)} + \mathrm{nH_2O}_{(ads)} \rightarrow \mathrm{Org}_{(ads)} + \mathrm{nH_2O}_{(sol)}$$

Where (n) is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. Attempts were made to fit (Θ) values to various isotherms, including Langmuir, Frumkin, Temkin and Freundlich isotherms. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by Eq (6) :

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

With

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \qquad (7)$$

where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant, ΔG°_{ads} is the standard free energy of adsorption, 55.5 is the concentration of water in the solution in mol

dm^{-3}, R is the universal gas constant and T is the absolute temperature in Kelvin. The plot of C_{inh} /Θ vs. C gives straight line (Fig. 5) (correlation > 0.998), the deviation of the slope from unity (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed inhibitor species [39].

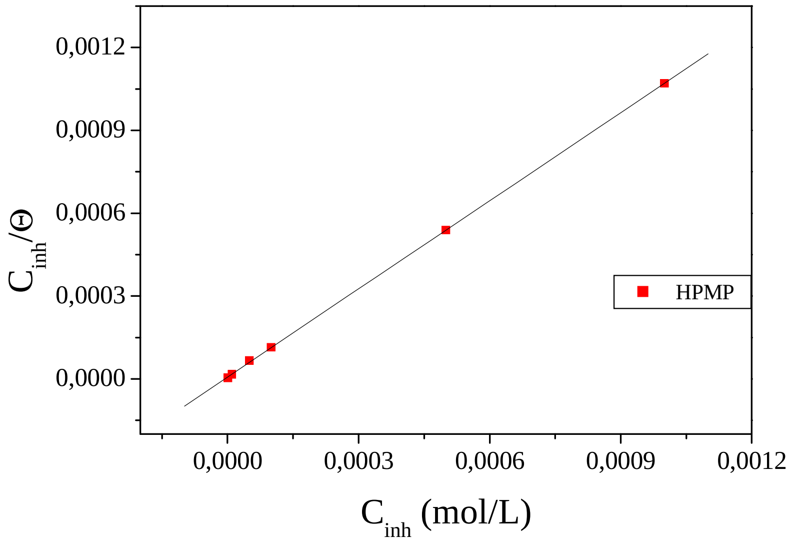

Fig. 5. Langmuir isotherm adsorption model of HPMP on the surface of copper in 2M HNO_3

The values of K_{ads} and ΔG°_{ads} were calculated at 303K and are listed in Table 2. The standard free energy of adsorption (ΔG°_{ads}), calculated from Eq. (7), is - 40.10 kJ mol^{-1} (K_{ads} = 147761.1 L mol^{-1}). The negative value of the standard free energy of adsorption and the high values of the adsorption constant indicate a spontaneous adsorption of this inhibitor on copper. Generally, the energy values of - 20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption; those of - 40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, chemisorption [40, 41]. The calculated ΔG°_{ads} value of slightly more negative than - 40 kJ mol^{-1} indicate, therefore, that the adsorption mechanism of the investigated HPMP on copper in 2M HNO_3 solution is typical of chemisorption (Table 2).

3.2.Electrochemical impedance spectroscopy

The corrosion behaviour of copper in 2M HNO_3 solution, in the absence and presence of HPMP, is also investigated by the EIS at 303 K after 30 min of immersion. The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [42]. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation:

$$C_{dl} = \left(\frac{1}{\omega R_t}\right) \qquad \text{where } \omega = 2\pi f_{\max} \tag{9}$$

The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_{R_t}\% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \qquad (10)$$

Where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of HPMP, respectively.

Fig. 6 shows Nyquist plots obtained from ac impedance measurements for copper in 2M HNO_3 in the presence of different concentrations of the inhibitor HPMP. Various parameters such as charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and f_{max} were obtained from impedance measurements and are shown in Table 3.

Table 3 Corrosion parameters obtained by impedance measurements for copper in 2M HNO_3 at various concentrations of HPMP.

Inhibitor	Conc (M)	R_t ($\Omega.cm^2$)	f_{max} (Hz)	C_{dl} ($\mu F/cm^2$)	E_{Rt} (%)
Blank	2	91.4	15.82	110.1	-
HPMP	10^{-3}	783.1	01.58	128,5	88.3
	10^{-4}	690.8	02.80	082.1	86.8
	10^{-5}	245.4	05.00	129.8	62.7
	10^{-6}	130.3	08.92	136.9	29.8

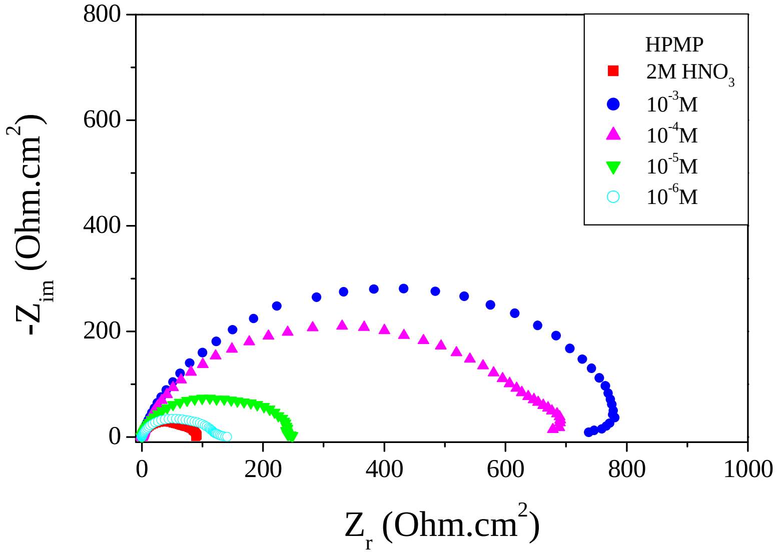

Fig. 6. Nyquist plots of copper in 2M HNO_3 containing various concentration of HPMP.

It is found (Table 3) that, as the HPMP concentration increases, the R_t values increase, but the C_{dl} values tend to decrease. The values of C_{dl} to HPMP, are superior to those obtained for blank. This increase can be attributed to a hydration of the film due to absorption of the electrolyte in the film. It is apparent from Nyquist diagrams that the charge-transfer resistance value of copper in uninhibited 2M HNO_3 solution changes significantly after the addition of the inhibitor. Furthermore, C_{dl} decreases with increase of the concentration of inhibitor. This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [43].

$$C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \qquad (5)$$

Where δ is the thickness of the protective layer, S is the electrode area, ε_o the vacuum permittivity of vide and ε is dielectric constant of the medium.

A low capacitance may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption [44]. The larger inhibitor molecules also reduce the capacitance through the increase in the double layer thickness [45]. The inhibiting effectiveness increases with the concentration of the inhibitor to reach a maximum value from 88.3 % to 10^{-3} M.

CONCLUSION

The following conclusions can be drawn from this study:

- All measurements showed that the pyridazine has excellent inhibition properties for the corrosion of copper in 2M HNO_3 solution. The weight loss measurements show that the inhibition efficiency decreases with increasing temperature and reaches its highest value (93.2 %) at 10^{-3} M concentration at 303K.
- The negative values of ΔG°_{ads} indicate that the adsorption of the inhibitor molecule is a spontaneous process and an adsorption mechanism is typical of chemisorption.
- The adsorption of HPMP on copper surface from 2M HNO_3 obeys the Langmuir adsorption isotherm.
- Impedance method indicates that HPMP adsorbs on the copper surface with increasing transfer resistance and decreasing of the double-layer capacitance.

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