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Investigation of the inhibition effect of 2-amino-4 methylphenylamine on corrosion of copper in 2.0 M HNO_3

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ABSTRACT

The corrosion behavior of copper in the presence of 2-amino-4-methylphenylamine (AMPA) has been investigated in 2.0 M HNO_3 *solution using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss techniques. Polarization studies showed that this compound act as mixed type inhibitor. Impedance spectroscopy measurement showed that the polarization resistance increased and that the capacitance decreased with the increase in the inhibitive concentration. The adsorption of this compound on the copper surface from the acid solution has been found to obey Langmuir adsorption isotherm. The thermodynamic activation parameters of copper corrosion in 2.0 M* HNO_3 *were determined and discussed. The results obtained from EIS, Tafel and weight loss measurements were in good agreement.*

Keywords: Inhibitor, Corrosion, Copper, EIS, Polarization studies, weight loss.

INTRODUCTION

The corrosion problems are of great interest for the industries because they are translated in great economic losses for them. Nowadays the research of novel inhibitors for metals or alloys is an important industrial and academic topic and the most efficient alternatives to protect metals and alloys from this phenomenon are the use of substances [1] that being adsorbed on metallic surface. It had been suggested [2,3] that most effective factors for inhibiting effects are the presence of polar atoms such as O, N, S, P, the unsaturated bonds, such as double bonds or triple bonds [4-16] and the plane conjugated systems including all kind of aromatic cycles [17-22] which can offer special active electrons or vacant orbital to donate or accept electrons.

A large number of organic molecules have at least one of the above-mentioned characteristics in their molecular structure according to diversity of organic compounds. The primary step [23] in the action of organic corrosion inhibitors in the solution is usually attributed to the adsorption process. Studies [24,25] report that adsorption process depends on the physico-chemical properties of the inhibitor molecule, related to the electronic density of donor atoms and on the possible steric effects.

Considerable attention has been drawn during the past few decades to inhibit corrosion of copper, as it has wide application in industry. Therefore, the purpose of the present paper is to investigate the inhibition behaviour of new compound AMPA for copper corrosion in 2.0 M HNO_3 solution. The corrosion protection effect of AMPA was investigated by means of weight loss measurement, potentiodynamic polarisation, and electrochemical impedance spectroscopy (EIS).

MATERIALS AND METHODS

The investigated 2-amino-4-methylphenylamine (AMPA) is obtained from Sigma-Aldrich chemical co. and its chemical structure is presented in Figure 1. The concentration range of the tested inhibitor employed was 1×10^{-5} M to 1×10^{-2} M. The material used in this study is a copper with a chemical composition (in wt%) of 0.01 % Ni, 0.019 % Al, 0.004 % Mn, 0.116 % Si and 99.5 % Cu Prolabo Chemicals. Prior to all measurements, the copper samples were pre-treated by grinding with emery paper SiC (180, 600 and 2000); rinsed with distilled water, degreased in ethanol in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (2.0 M HNO_3) were prepared by dilution of an analytical reagent grade 65% HNO_3 with doubly distilled water.

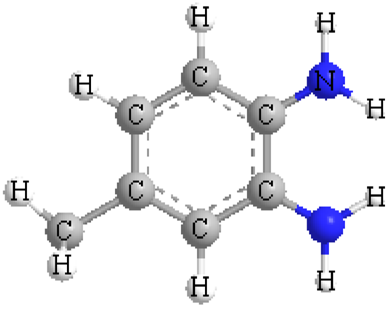

Figure 1. The chemical structure of the studied inhibitor.

The gravimetric measurements were carried out at the definite time interval of 1 h at room temperature using an analytical balance (precision ± 0.1 mg). Each run was carried out in a glass vessel containing 100 mL of the test solution. A clean weighed copper electrode (2 × 2 × 0.2 cm^3) was completely immersed at inclined position in the vessel. After the exposure time, the electrode was withdrawn, rinsed with doubly distilled water, washed with ethanol, dried and weighed. Two batches of tests were performed, and the data reported in this paper represent the average value of the two tests. The weight loss (w), in mg, was taken as the difference in the weight of the copper coupons before and after immersion in different test solutions. Weight loss allowed calculation of the mean corrosion rate (C_R) in mg cm^{-2} h^{-1}.

Electrochemical measurements were carried out in a conventional three-electrode cylindrical Pyrex glass cell. All electrochemical tests have been performed at 303 K in non-de-aerated solutions The working electrode (WE) in the form of disc cut from copper has a geometric area of 0.28 cm^2 and is embedded in polytetrafluoroethylene (PTFE). A saturated calomel electrode (SCE) and a platinum electrode were used, as reference and auxiliary electrodes, respectively. A fine Luggin capillary was placed close to the working electrode to minimize ohmic resistance. The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained.

Electrochemical impedance spectroscopy experiments were conducted using Tacussel-Radiometer PGZ 301 and Voltamaster.4 Software was used to run the tests and to collect the experimental data. Ac impedance measurements were carried-out in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments.

Potentiodynamic polarization experiments were conducted using an electrochemical measurement system Tacussel Radiometer PGZ 301 controlled by a PC supported by Voltamaster.4 Software. The polarization curve was recorded by polarization from -150 to 150 mV versus E_{ocp} with a scan rate of 1 mV s^{-1} under air atmosphere**.**

RESULTS AND DISCUSSION

Weight loss measurements

Effect of concentration

The inhibition effect of the investigated 2-amino-4-methylphenylamine (AMPA) at different concentrations on the corrosion of copper in 2.0 M HNO_3 solution was studied by weight loss measurements at 303 K after 1 h of immersion period. The corrosion rate (C_R) and inhibition efficiency, $\eta_{WL}(\%)$, were calculated according to the Eqs. 1 and 2, [26, 27] respectively:

$$C_R = \frac{W_b - W_a}{At} \qquad (1)$$

$$\eta_{\mathrm{WL}}(\%) = \left(1 - \frac{wi}{w_0}\right) \times 100 \tag{2}$$

where W_b and W_a are the specimen weight before and after immersion in the tested solution, w_0 and w_i are the values of corrosion weight losses of copper in uninhibited and inhibited solutions, respectively, A the area of the copper specimen (cm^2) and t is the exposure time (h).

The values of percentage inhibition efficiency (η_{WL} %) and corrosion rate (C_R) obtained from weight loss method at different concentrations of AMPA at 303 K are summarized in Table 1.

Table 1. Corrosion parameters obtained from weight loss measurements for copper in 2.0 M HNO_3 containing various concentrations of AMPA at 303 K.

C_{inh} (M)	C_R (mg cm^{-2} h^{-1})	η_{WL} (%)
Blank	1.780	-----
1×10^{-5}	1.594	10.4
1×10^{-4}	1.454	18.3
5×10^{-4}	1.022	42.6
1×10^{-3}	0.821	53.9
5×10^{-3}	0.654	63.3
1×10^{-2}	0.590	66.9

From table 1 the measurements for different concentrations of amine derivative show that this inhibitor inhibits the corrosion of copper. Corrosion rate values of copper decrease when the inhibitor concentration increases. The inhibition efficiency η_{WL} (%) increases with increasing inhibitor concentration. At 10^{-2} M for each inhibitor studied, the inhibition efficiency attains 67%.

Effect of temperature

Temperature can affect the steel corrosion in the acidic media in the presence and absence of inhibitor. Generally the corrosion rate increases with the rise of the temperature. To determine the action energy of the corrosion process, gravimetric measurements are taken at various temperatures (303-343 K) in the absence and presence of inhibitor at 10^{-2} M after 1 h of immersion.

The corresponding results are given in Table 2. It is clear that the increase of corrosion rate is more pronounced with the rise of temperature for the blank solution. In the presence of the tested molecules, corrosion rate is reduced even at high temperature. η_{WL} (%) passed from 66.9 to 12.9% when temperature rises from 303 to 343 K at 10^{-2} M of this compound. We note that the efficiency of the inhibitor tested depends on the temperature and decreases with the rise of temperature from 303 to 343 K.

Table 2. Various corrosion parameters for copper in 2.0 M HNO_3 in absence and presence of optimum concentration of AMPA at different temperatures.

Temp (K)	Inhibitor	C_R (mg cm^{-2} h^{-1})	η_{WL} (%)	θ
303	Blank	1.780	------	------
	AMPA	0.590	66.9	0.669
313	Blank	7.333	------	------
	AMPA	2.884	60.7	0.607
323	Blank	24.97	------	------
	AMPA	11.52	53.9	0.539
333	Blank	70.82	------	------
	AMPA	46.27	34.7	0.347
343	Blank	186.6	------	------
	AMPA	162.6	12.9	0.129

The activation thermodynamic parameters of the corrosion process were calculated from Arrhenius Eq. (3) and transition state Eq. (4) [28]:

$$C_R = k \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \tag{4}$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, k is the Arrhenius pre-exponential factor, h is Plank's constant, N is Avogrado's number, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

Figure 2 presents the Arrhenius plots of the natural logarithm of the corrosion rate vs. 1/T for copper in 2.0 M HNO_3 without and with addition of AMPA. The calculated values of activation energy are given in Table 3. The data show that the activation energy (E_a) of the corrosion in copper in 2.0 M HNO_3 solution in the presence of this compound is higher than that in the free acid solution. The increase in the apparent activation energy for copper dissolution in inhibited solution may be interpreted as physical adsorption that occurs in the first stage [29]. Szauer and Brand explained [30] 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.

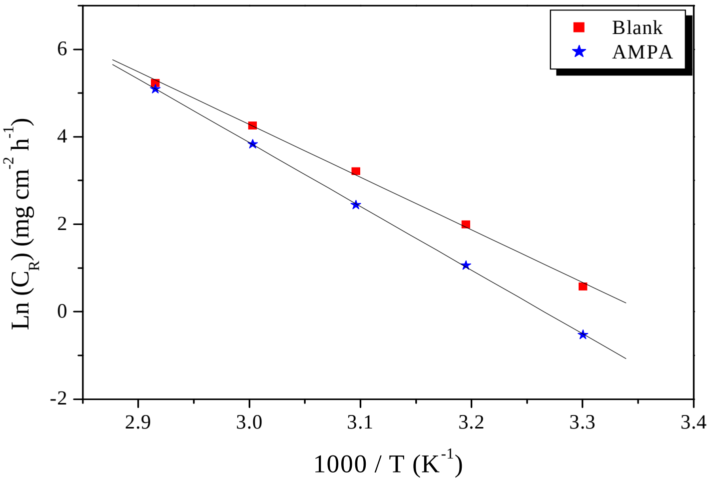

Figure 2. Arrhenius plots of Ln C_R vs. 1/T for copper in 2.0 M HNO_3 in the absence and the presence of AMPA at optimum concentration.

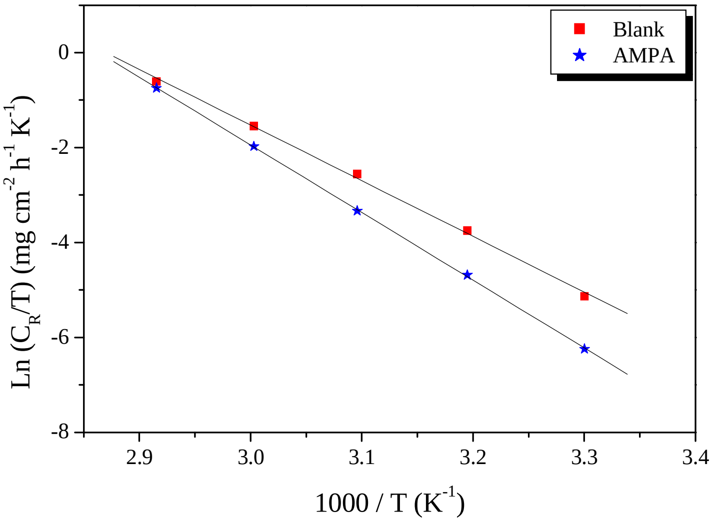

Figure 3. Arrhenius plots of Ln (C_R /T) vs. 1/T for copper in 2.0 M HNO_3 in the absence and the presence of AMPA at optimum concentration.

Figure 3 shows a plot of Ln(C_R/T) against $1/T$. A straight lines are obtained with a slope of ($-\Delta H_a/R$) and an intercept of (Ln $R/Nh + \Delta S_a/R$) from which the values of ΔH_a and ΔS_a are calculated and are listed in Table 3. Inspection of these data reveals that the ΔH_a value for dissolution reaction of copper in 2.0 M HNO_3 in the presence of AMPA is higher than that of in the absence of inhibitor. The positive signs of ΔH_a reflect the endothermic nature of the copper dissolution process suggesting that the dissolution of copper is slow in the presence of inhibitor [31].

In addition, the value of ΔS_a was higher for inhibited solutions than that for the uninhibited solution (Table 3). This suggested that an increase in randomness occurred on going from reactants to the activated complex. Thus the increasing in entropy of activation was attributed to the increasing in solvent entropy [32].

Table 3. Corrosion kinetic parameters for copper in 2.0 M HNO_3 at 303K of AMPA

Inhibitor	k (mg cm^{-2} h^{-1})	Linear regression coefficient (r)	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol K)
Blank	3.663×10^{17}	0.999	100.21	97.53	82.36
AMPA	4.652×10^{20}	0.999	121.17	118.49	141.78

Adsorption isotherm

The interactions between the extracts and the copper surface can be examined by the adsorption isotherm. The inhibition efficiency is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ), which was calculated in this case using the equation $\theta = \eta_{WL}$ (%)/100. The adsorption isotherms most frequently used are Langmuir, Temkin, Frumkin and Flory-Huggins. Therefore, each of these adsorption isotherms was tested for its ability to describe the adsorption behavior of extracts on a copper surface in an HNO_3 solution. The coefficient of determination (R^2) was considered to choose the isotherm that best fitted the experimental data. The linear relationships of C/θ vs. C, shown in Figure 4, suggest that the adsorption of AMPA on the copper obeyed the Langmuir adsorption isotherm. This isotherm can be represented as:

$$\frac{C}{\theta}=\frac{1}{K}+C \tag{5}$$

where K is the adsorption constant, C is the concentration of the inhibitor and surface coverage values (θ) are obtained from the weight loss measurements for various concentrations. Plots of C/θ versus C yield a straight line as shown in Fig. 4. In both cases the linear regression coefficients (R^2) are almost equal to 1 and the slopes is very close to 1, indicating that the adsorption of AMPA in 2.0 M HNO_3 follows the Langmuir isotherm and exhibit single-layer adsorption characteristic. According to Eq. 5, K can be calculated from intercept on the C/θ axis. By use of the equation below, ΔG°_{ads} can be calculated from K.

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \tag{6}$$

Where R is gas constant and T is absolute temperature of experiment and the constant value of 55.5 is the concentration of water in solution in mol L^{-1}. The thermodynamics parameters derived from Langmuir adsorption isotherm for the studied compound, are given in Table 4.

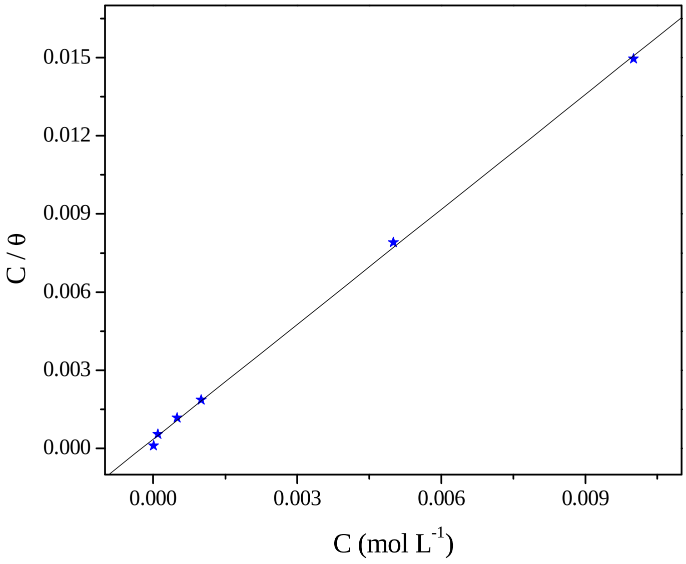

Figure 4. Langmuir adsorption of AMPA on the copper surface in 2.0 HNO_3 solution.

Table 4. Thermodynamic parameters for the adsorption of AMPA in 2.0 HNO_3 on the copper at 303K.

Inhibitor	K (M^{-1})	R^2	ΔG°_{ads} (kJ/mol)
AMPA	2869.01	0.99961	-30.17

The values of ΔG°_{ads} was also listed in Table 4. The negative values of ΔG°_{ads} suggest that the adsorption of AMPA is a spontaneous process. Generally speaking, values of ΔG°_{ads} up to -20 kJ mol^{-1} indicate the electrostatic attraction between the charged metal surface and charged organic molecules in the bulk of the solution (physisorption). Those around -40 kJ mol^{-1} or smaller involve charge sharing or charge transfer between the metal and the organic molecules (chemisorption) [33]. The calculated ΔG°_{ads} value for AMPA is between -40 kJ mol^{-1} and -20 kJ mol^{-1} ,indicating that the adsorption mechanism of this compound on copper in a 2.0 M nitric acid solution at 303K was a combination of both physisorption and chemisorptions.

Polarization measurements

The effect of the concentration of AMPA is shown in Fig.5 which presents the anodic and cathodic Tafel curves of copper in 2.0 M HNO_3. Values of cathodic β_c Tafel constant and corrosion current density are listed in Table 5. These values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at E_{corr}. The inhibition efficiencies are calculated by the following expression:

$$E_I\,(\%) = \frac{I_{\mathrm{corr}} - I_{\mathrm{corr(inh)}}}{I_{\mathrm{corr}}} \times 100 \qquad (7)$$

where I_{corr} and $I_{\mathrm{corr(inh)}}$ are the corrosion current densities for copper electrode in the uninhibited and inhibited solutions, respectively.

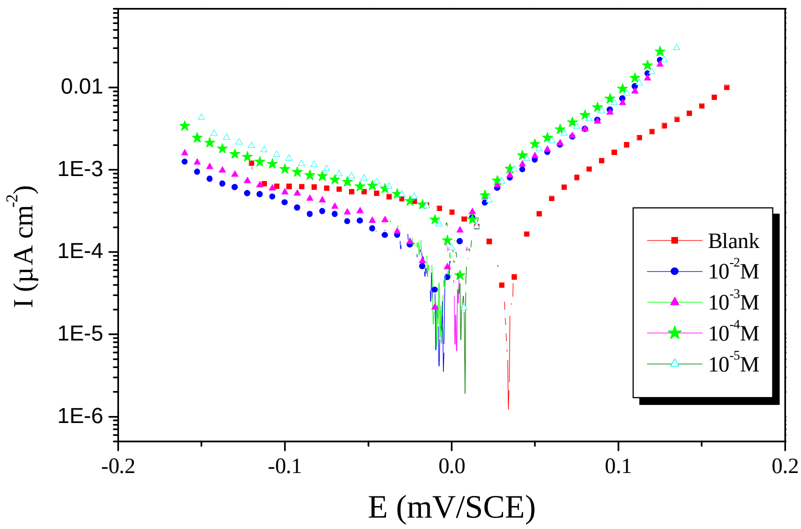

Figure 5. Polarisation curves of copper in 2.0 M HNO_3 for various concentrations of AMPA.

It is evident from Table 5 and Figure 5 that the value of β_c changed with increase in inhibitor concentration and indicates the influence of the inhibitor on the kinetics of the hydrogen evolution. The corrosion current density (I_{corr}) decreased by the increase in the adsorption of the inhibitor with increasing inhibitor concentration. According to Ferreira et.al [34] and Li et. al. [35], if the displacement in corrosion potential is more than 85 mV with respect to the corrosion potential of the blank solution, the inhibitor can be consider as a cathodic or anodic type. In present study, maximum displacement was 42.2 mV with respect to the corrosion potential of the uninhibited sample which indicates that the studied inhibitor is a mixed type of inhibitor.

Table 5. Polarization data of copper in 2.0 M HNO_3 without and with addition of inhibitor at 303K.

Inhibitor	Conc (M)	E_{corr} (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu A\ cm^{-2}$)	E_I (%)
Blank	2.0	34.0	304.7	365.1	-
AMPA	10^{-2}	-08.2	173.1	121.8	66.6
	10^{-3}	-08.1	174.6	157.9	56.8
	10^{-4}	1.50	183.9	290.7	20.4
	10^{-5}	5.80	162.1	318.2	12.8

Electrochemical impedance spectroscopy

Figure 6 shows the impedance spectra of copper obtained at open-circuit potential after an exposure period of 30 min in 2.0 M HNO_3 solution in the absence and presence of different concentrations of AMPA at 303 K.

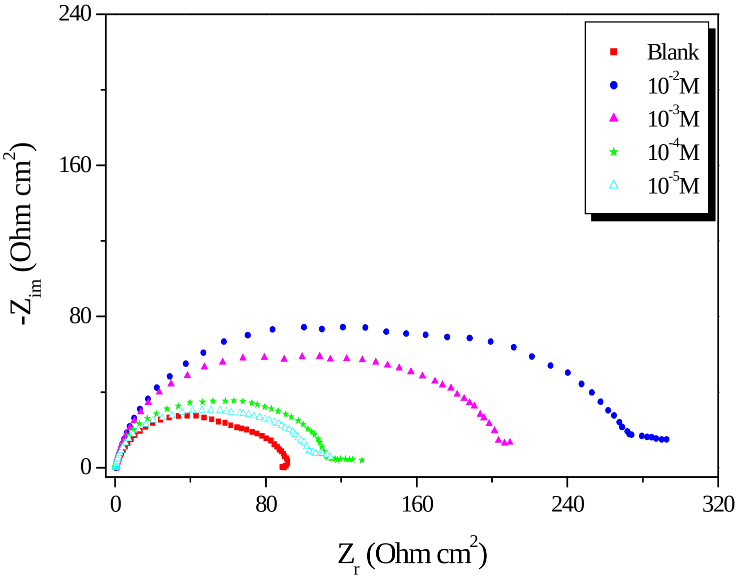

Figure 6. Nyquist plots for copper in 2.0 M HNO_3 in the absence and presence of different concentrations of AMPA at 303K.

The analysis of Figure 6 shows that AMPA inhibits the nitric acid corrosion of copper. Indeed, the presence of AMPA increases the impedance (i.e., size of the capacitive loop) with increasing of inhibitor concentration. The increase in the size of the capacitive loop with the addition of AMPA molecules show that a barrier gradually forms on the copper surface. The barrier is probably related to the formation of an inhibitor surface film through its adsorption on the copper surface. The recorded impedance spectra are, in all cases, characterized by the appearance of two clearly resolved time constants related to the both capacitive loops, the first loop in high frequency (HF) range and the second one in the low frequency (LF) range. The first capacitive loop can be related to charge-transfer in corrosion process [36]. The depressed form of the higher frequency loop reflects the surface inhomogeneity of structural or interfacial origin, such as those found in adsorption processes [37]. The presence of the second capacitive loop may be attributed to the adsorption of inhibitor molecules on the metal surface and/or all other accumulated kinds at the metal/solution interface (inhibitor molecules, corrosion products, etc.) [38].

It is well-known that it is essential to develop the appropriate models for the impedance which can then be used to fit the experimental data and extract the parameters which characterize the corrosion process. Indeed, we tried with many suggested equivalent circuits to fit our impedance data using computer program EQUIVCRT [39]. For these reasons, the total resistance (polarization resistance, R_p) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [40], using a non-linear least square fit “fit circle option” (Table 6). The related inhibition efficiency, $\eta_Z(\%)$, is calculated from R_p using the following equation:

$$\eta_Z(\%) = \frac{R_{P(i)} - R_p}{R_{P(i)}} \times 100 \qquad (8)$$

where R_p and $R_{p(i)}$ are the ac polarisation resistance of copper electrode in the uninhibited and inhibited solutions, respectively. To obtain the capacitance (C) the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in the following equation [40]:

$$C = \frac{1}{2\pi f_{max} R_P}$$

Table 6. Impedance parameters and inhibition efficiency values for copper in 2.0 M HNO_3 containing different concentrations of AMPA at 303 K

Inhibitor	Conc (M)	R_p (Ω cm^2)	f_{max} (Hz)	C (µF cm^{-2})	η_z (%)
Blank	2.0	091.41	15.82	110.11	-----
AMPA	10^{-2}	274.3	07.14	081.3	66.7
	10^{-3}	207.6	08.92	085.9	56.0
	10^{-4}	113.7	14.04	099.7	19.6
	10^{-5}	106.2	14.04	106.7	13.9

The analysis of the electrochemical parameters shows that the R_p value increases when the AMPA concentration increases, giving consequently a decrease in the corrosion rate. It is important to emphasize that the values of capacitance (C) decrease with increasing concentration of inhibitor. The inhibition efficiency $\eta_Z(\%)$ is also found to increase with the concentration of AMPA, reaching its maximum value at 10^{-2} M.

CONCLUSION

2-amino-4-methylphenylamine (AMPA) acts as an inhibitor for corrosion of copper in 2.0 M HNO_3 solution. EIS measurements also indicates that the inhibitor performance increase due to the adsorption of molecules on the metal surface. Potentiodynamic polarization measurements showed that the inhibitor acts as mixed type of inhibitor. The inhibitor showed maximum inhibition efficiency (approx 67%) at 10^{-2} M concentration of the studied inhibitor. The inhibition efficiency of AMPA decreased with temperature, which leads to an increase in activation energy of corrosion process. The adsorption of 2-amino-4-methylphenylamine follows Langmuir`s adsorption isotherm. The adsorption process is spontaneous and exothermic, accompanied by an increase of entropy. The results obtained from different experimental studies are in good agreement.

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