Research Article

Electrochemical Investigations of Pyridine-2-Carbaldehyde Derivatives as Potential Inhibitors against Copper Corrosion in 0.1M HNO_3

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ABSTRACT

The corrosion inhibition efficiency of Pyridine-2-carbaldehyde-2-aminobenzoic acid (2PC2ABA) and Pyridine-2-carbaldehyde-3-aminobenzoic acid (2PC3ABA) on copper in 0.1M HNO_3 solution has been investigated and compared using electrochemical impedance spectroscopy, adsorption studies and potentiodynamic polarization analysis. The pyridine-2-carbaldehyde derivatives exhibited very good corrosion inhibition on copper in HNO_3 medium and the inhibition efficiency increased with the increase in concentration of the inhibitor. The adsorption of the inhibitor on the surface of the corroding metal obeys Langmuir and El-Awady adsorption isotherm for 2PC2ABA and 2PC3ABA respectively. Thermodynamic parameters (K_{ads}, ΔG^0_{ads}) were calculated using adsorption isotherm. Polarization studies revealed that both compound act as a mixed type inhibitor.

Keywords: Corrosion inhibitors, Isotherm, pyridine-2-carbaldehyde, El-Awady, Langmuir

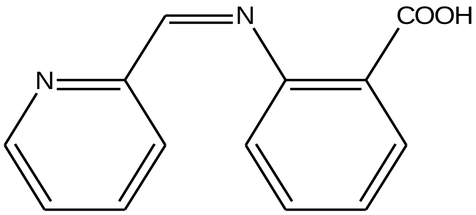
1. INTRODUCTION

One of the most practical methods for the protection against corrosion in acidic media is the use of chemical inhibitors. Most of the excellent acid inhibitors are organic compounds containing nitrogen, oxygen, phosphorus and sulphur. Due to the presence of C=N- group and electronegative N, S or O atoms in the molecule, should be good corrosion inhibitors [1-4]. Organic compounds containing functional electronegative groups and π electrons in triple or conjugated double bonds such as nitrogen, sulphur, and oxygen are usually good inhibitors since these compounds are easily adsorbed on metal surfaces. Studies on the relation between adsorption and corrosion inhibition are of considerable importance. The action of such inhibitors depends on the specific interaction between the functional groups and the metal surface. Corrosion commonly occurs at metal surfaces in the presence of oxygen and moisture, involving electrochemical reactions [5-7]. The application of heterocyclic derivatives as an effective corrosion inhibitor is mainly based on their ability to form a monolayer on the surface of the corroding material. Increasing efforts have been made to study the corrosion behaviour of metals and mechanism of inhibition during the past decade mainly through electrochemical investigations [8-11].

In the present course of studies the corrosion inhibiting behavior of two heterocyclic derivatives, pyridine-2-carbaldehyde-2-aminobenzoic acid (2PC2ABA) and pyridine-2-carbaldehyde-3-aminobenzoic acid (2PC3ABA) were investigated on copper in 0.1M HNO_3 solutions using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization analysis and adsorption studies.

2. EXPERIMENTAL ANALYSIS

All the chemicals used were of analytical grade and solvents used for spectral studies were of spectroscopic grade. The heterocyclic derivatives such as pyridine-2-carbaldehyde-2-aminobenzoic acid (2PC2ABA) and pyridine-2-carbaldehyde-3-aminobenzoic acid (2PC3ABA) were prepared by the following method. The condensation of equimolar mixtures of Pyridine-2-carbaldehyde and 2-aminobenzoic acid/3-aminobenzoic acid in ethanol medium under reflux condition for 4h. The mixture was cooled in ice and precipitate was filtered, washed with ethanol water mixture (1:1) and dried. The compounds were characterized by spectroscopic tools like IR, UV, ^{1}H NMR and ^{13}C NMR and mass Figure1a and 1b shows the molecular structure of the heterocyclic compounds 2PC2ABA and 2PC3ABA.



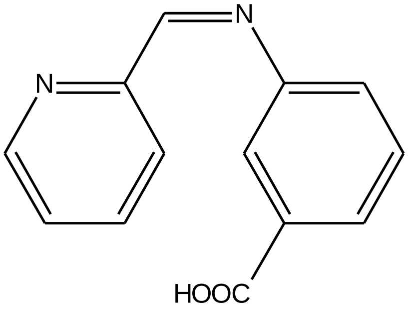


Figure 1a: Molecular Structure of 2PC2ABA **Figure 1b:** Molecular Structure of 2PC3ABA

Electrochemical impedance spectroscopy (EIS). The EIS measurements were performed in a three electrode assembly. Saturated calomel electrode (SCE) was used as the reference electrode. Platinum electrode having 1cm^2 area was taken as counter electrode. Metal specimens with an exposed area of 1cm^2 were used as the working electrode. The EIS experiments were carried out on an Ivium compactstat-e electrochemical system. 0.1M HNO_3 was taken as the electrolyte and the working area of the metal specimens were exposed to the electrolyte for 1 h prior to the measurement. EIS measurements were performed at constant potential (OCP) in the frequency range from 1 KHz to 100 mHz with amplitude of 10 mV as excitation signal. The percentage of inhibitions from impedance measurements were calculated using charge transfer resistance values by the following expression [1]

$$\eta_{EIS}\,\% = \frac{R_{ct} - R'_{ct}}{R_{ct}}\, X100$$

(1) where R_{ct} and R'_{ct} are the charge transfer resistances of working electrode with and without inhibitor respectively.

Potentiodynamic polarization. Electrochemical polarization studies were performed by recording anodic and cathodic potentiodynamic polarization curves. Polarization plots were obtained in the electrode potential range from -250 to +250 mV Vs corrosion potential (E_{corr}) at a scan rate of 1mV/sec. Tafel polarization analysis were done by extrapolating anodic and cathodic curves to the potential axis to obtain corrosion current densities(I_{corr}). The percentage of inhibition efficiency ($\eta_{pol}\%$) was evaluated from the measured I_{corr} values using the following relation [12]

$$\eta_{pol}\,\% = \frac{I_{corr} - I'_{corr}}{I_{corr}}\, X100 \qquad (2)$$

where I_{corr} and I'_{corr} are the corrosion current densities of the exposed area of the working electrode in the absence and presence of inhibitor respectively. From the slope analysis of the linear polarization curves in the vicinity of corrosion potential of blank and different concentrations of the inhibitor, the values of polarization resistance (R_p) in 0.1M HNO_3 solution were obtained. From the evaluated polarization resistance, the inhibition efficiency was calculated using the relationship

$$\eta_{R_p}\,\% = \frac{R'_p - R_p}{R'_p}\, X100$$

(3) where R'_p and R_p are the polarization resistance in the presence and absence of the inhibitor respectively [1].

3. RESULTS AND DISCUSSIONS

Electrochemical impedance spectroscopy. Figure 2a and 2b represents the Nyquist plots of 2PC2ABA and 2PC3ABA of copper specimens in 0.1M HNO_3. It is evident from the plots that the impedance response of metal specimens showed a marked difference in the presence and absence of the heterocyclic derivatives. The capacitance loop intersects the real axis at higher and lower frequencies. At high frequency end, the intercept corresponds to the solution resistance (R_s) and at lower frequency end, corresponds to the sum of R_s and charge transfer resistance (R_{ct}). The difference between the two values gives R_{ct} [13-15]. The value of R_{ct} is a measure of electron transfer across the exposed area of the metal surface and it is inversely proportional to rate of corrosion [16-18].

Table 1: Electrochemical Impedance parameters of copper specimens in 0.1M HNO_3 in the absence and presence of 2PC2ABA and 2PC3ABA

Heterocyclic derivatives	Conc. (mM)	C_{dl} (μFcm^{-2})	R_{ct} (Ωcm^2)	$\eta_{EIS\%}$
	0	745	135.9	-
2PCOABA	0.2	112	2147	93.6
	0.4	66	3578	96.2
	0.6	70	3844	96.4
	0.8	76	3862	96.4
	1.0	67	5147	97.3
2PCMABA	0.2	585	188.6	27.9
	0.4	744	417	67.4
	0.6	170	480	71.6
	0.8	114	1334	89.8
	1.0	99	1545	91.2

Impedance behavior can be well explained by pure electric models that could verify and enable to calculate numerical values corresponding to the physical and chemical properties of electrochemical system under examination. The simple equivalent circuit that fit to many electrochemical system composed of a double layer capacitance, R_s and R_{ct} [19, 20]. To reduce the effects due to surface irregularities of metal, constant phase element (CPE) is introduced into the circuit instead of a pure double layer capacitance [21] which gives more accurate fit as shown in the Figure 3.

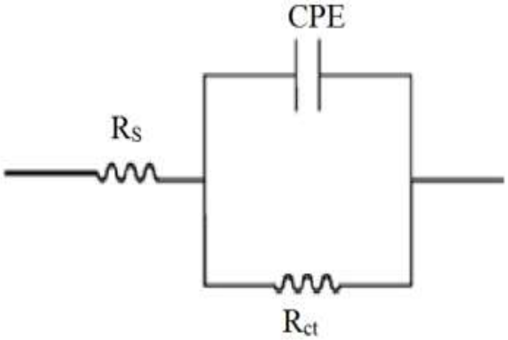


Figure 3: Equivalent circuit fitting for EIS measurements

The impedance of CPE can be expressed as $Z_{CPE} = \frac{1}{Y_0 \ (j\omega)^n}$ (4)

where Y_0 is the magnitude of CPE, n is the exponent (phase shift), ω is the angular frequency and j is the imaginary unit. CPE may be resistance, capacitance and inductance depending upon the values of n [22]. The EIS parameters such as R_{ct}, R_s and CPE and the calculated values of percentage of inhibition ($\eta_{EIS\%}$) of copper specimens are listed in Table 1. The R_{ct} values are increased with increasing inhibitor concentration. Decrease in capacitance values CPE with inhibitor concentration can be attributed to the decrease in local dielectric constant and /or increase in the thickness of the electrical double layer. This emphasis the action of inhibitor molecules by adsorption at the metal–solution interface [23]. The percentage of inhibition ($\eta_{EIS\ \%}$) showed a regular increase with increase in inhibitor concentration. Electrochemical impedance studies showed that the impedance behavior of copper has significantly altered by the addition of 2PC2ABA and 2PC3ABA to the corroding medium. R_{ct} values are greater for uninhibited one and the impedance of inhibited systems increased with the increase in concentration of organic molecules in nitric acid. The inhibition efficiencies of 2PC2ABA on copper surface are significantly greater than that of 2PC3ABA at all concentrations. Even at a lower concentration of 0.2mM, the former one showed 93% inhibition response on the copper surface in nitric acid medium.

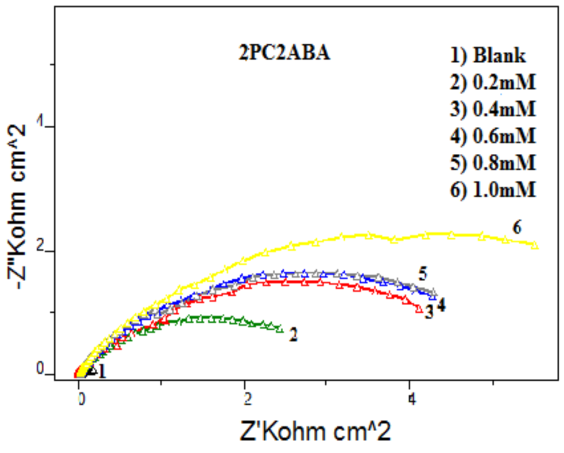


Figure 2a: Nyquist plots for copper specimens in the presence and absence of 2PC2ABA.

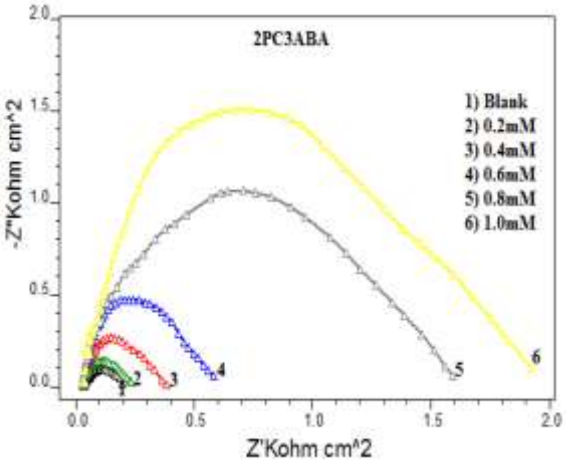


Figure 2b: Nyquist plots for copper specimens in the presence and absence of 2PC3ABA.

***Adsorption isotherm and free energy of adsorption*.** The mechanism of adsorption and the surface behaviour of organic molecules can be easily viewed through adsorption isotherms. Different models of adsorption isotherms considered are Langmuir, Temkin, Frumkin, El-Awady, Flory-Huggin and Freundlich isotherms. For the evaluation of thermodynamic parameters it is necessary to determine the best fit isotherm with the aid of correlation coefficient (R^2). Table 2 contains the adsorption isotherm and their regression coefficients for 2PC2ABA and 2PC3ABA on copper in 0.1M HNO_3. Langmuir adsorption isotherm fits well the experimental data for 2PC2ABA and El-Awady adsorption isotherm for 2PC3ABA on copper specimens in 0.1M HNO_3. This can be expressed as,

Langmuir adsorption isotherm $\frac{C}{\theta} = \frac{1}{K_{ads}} + C$ (5)

El-Awady adsorption isotherm $\log(\theta/1-\theta) = \log K + y\log C$ (6)

Where C is the concentration of the inhibitor, θ is the fractional surface coverage and K_{ads} is the adsorption equilibrium constant [24]. Figure 4a and 4b represents the Langmuir adsorption isotherm and El-Awady adsorption isotherm for 2PC2ABA and 2PC3ABA respectively. The K_{ads} is related to the standard free energy of adsorption ΔG^0_{ads}, by

$$\Delta G^0_{ads} = -RT\ln(55.5\ K_{ads}) \qquad (7)$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in Kelvin [25]. The negative value of free energy of adsorption indicates the spontaneity of the process. In the present investigation 2PC2ABA and 2PC3ABA molecules showed ΔG^0_{ads} -39.13 and -30.24 respectively for copper specimens suggesting that the adsorption of 2PC2ABA molecules involved chemisorptions and 2PC3ABA involved both physisorption and chemisorptions. [26]

Table 2 Adsorption isotherm and their regression Coefficients for 2PC2ABA and 2PC3ABA on in 0.1M HNO_3

Adsorption isotherm	Regression coefficient	
	2PC2ABA	2PC3ABA
Langmuir	0.999	0.780
Freundlich	0.755	0.846
Frumkin	0.940	0.934
Temkin	0.887	0.953
El-Awady	0.905	0.960
Flory-Huggin	0.901	0.572

Table 3 Thermodynamic parameters obtained from adsorption of 2PC2ABA and 2PC3ABA

Inhibitor	K_{ads}	ΔG^0_{ads} (kJ/mol)
2PC2ABA	111111	-39.13
2PC3ABA	3199	-30.24

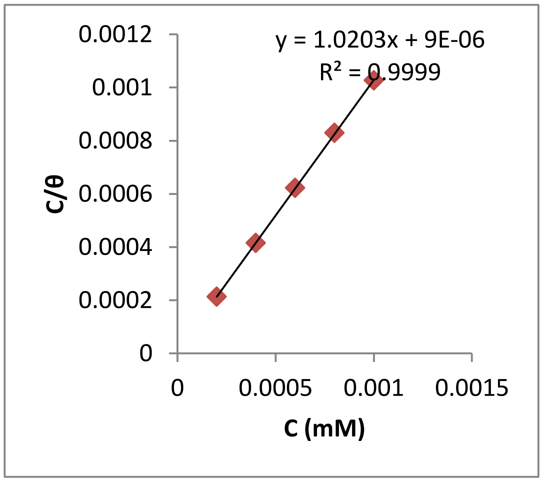


Figure 4a: Langmuir adsorption isotherm for 2PC2ABA on copper surface in 0.1M HNO_3

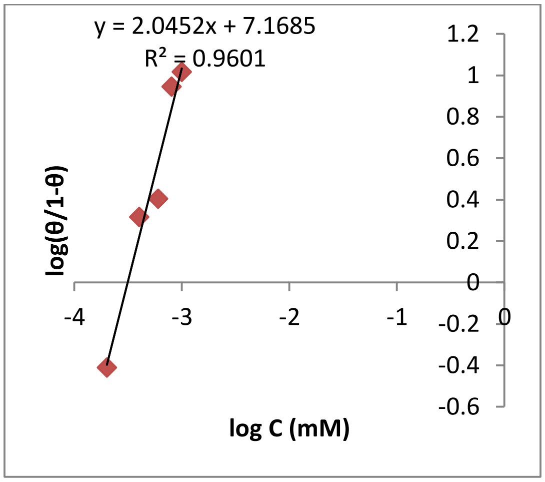


Figure 4b: El-Awady adsorption isotherm for 2PC3ABA on copper surface in 0.1M HNO_3

Potentiodynamic polarization studies. Tafel polarization curves for 2PC2ABA and 2PC3ABA are shown in Figure.5a and 5b. Polarization parameters like corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), and inhibition efficiency (E_P) for copper specimens are listed in Table 4. A prominent decrease in the corrosion current density (I_{corr}) was observed in the presence of inhibitor molecules. A lowest value of I_{corr} was noticed for the inhibitor solution of concentration 1mM which exhibited a maximum inhibition efficiency of 96%. Since the value of b_c changes appreciably in the presence of 2PC3ABA, it may be assumed that the inhibitor molecules are more adsorbed on cathodic sites. On close examination of the Tafel plots and polarisation parameters of 2PC2ABA it may be concluded that the corrosion potentials of copper at various concentrations of 2PC2ABA changes to cathodic and anodic directions and the inhibitive activity of this molecule can be regarded as a mixed type, that is 2PC2ABA affect both cathodic and anodic process of corrosion more or less uniformly. Also the cathodic and anodic slopes of the Tafel curve changes in each scans, which can be taken as an additional supporting evidence for the above argument. The 2PC3ABA molecule can also be regarded as the mixed type inhibitor, but predominantly affect on cathodic site. These results are in good agreement with the results obtained by impedance analysis.

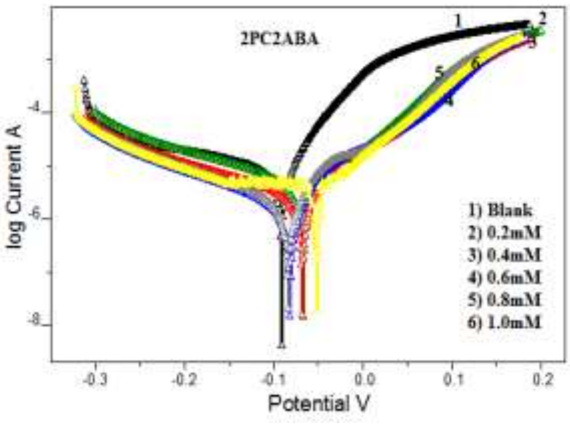


Figure 5a: Tafel plots of copper Specimens with and without inhibitor 2PC2ABA

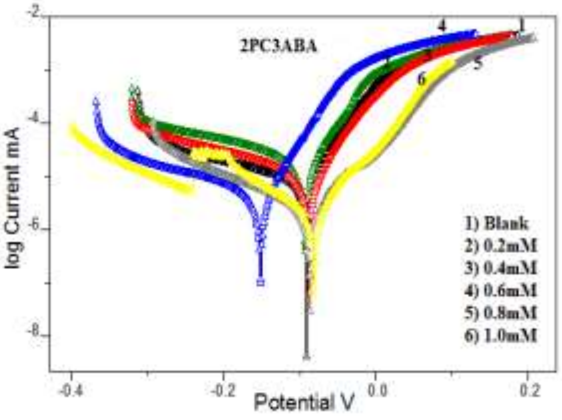


Figure 5b: Tafel plots of copper Specimens with and without inhibitor 2PC3ABA

Table 4: Potentiodynamic polarization parameters of copper specimens in 0.1M HNO_3 in the absence and presence of 2PC2ABA and 2PC3ABA.

Inhibitors	Tafel Data						Linear Polarization Data	
	Conc. (mM)	E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	b_a (mv/dec)	$-b_c$ (mV/dec)	$\eta_{pol\%}$	R_p (ohm)	$\eta_{Rp\%}$
2PC2ABA	0	-240	27.0	168	309	-	1758	-
	0.2	-49	3.8	68	211	85	4659	56
	0.4	-54	2.1	72	195	92	6094	71
	0.6	-79	1.6	82	172	93	7605	76
	0.8	-63	1.4	63	163	94	9259	81
	1.0	-67	1.0	65	150	96	11252	84
2PC3ABA	0.2	-236	65	202	215	-143	910	-93
	0.4	-166	24	128	295	10	1767	0.5
	0.6	-286	17	147	269	37	3243	45
	0.8	-80	2.4	68	177	91	6500	72
	1.0	-120	1.6	78	154	94	7170	75

4. CONCLUSION

This work establishes the comparison of anticorrosive properties of two novel heterocyclic derivatives 2PC2ABA and 2PC3ABA on copper in 0.1MHNO$_3$. The molecules 2PC2ABA and 2PC3ABA showed inhibition efficiency 27% and 93% respectively for a concentration of 0.2mM by electrochemical impedance study. Corrosion inhibition efficiency of 2PC2ABA and 2PC3ABA are in good agreement with EIS studies and potentiodynamic polarization studies. The inhibition mechanism is explained by adsorption. The molecules 2PC2ABA and 2PC3ABA obeyed Langmuir isotherm and El-Awady adsorption isotherm respectively on copper surface. The thermodynamic parameters of the adsorption are calculated from the adsorption isotherms which showed that both physisorption and chemisorption are involved in the inhibition process.

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