



Corrosion Inhibition of Mild Steel in HCl by Isolated Compounds of *Ricinus Communis* (L.)

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Abstract: We have isolated three pyridine base alkaloids namely ricinine (C1), *N*-demethylricinine (C2) and 4-methoxy pyridine-3-carboxylic acid (C3) from methanolic extract of *Ricinus Communis* leaves and investigated corrosion inhibition effect on mild steel in 0.5 HCl solution using the weight loss and electrochemical techniques (Galvanostatic polarization and EIS). Polarization resistances calculated from the EIS measurements are in good agreement with those obtained from alternating current (AC) polarization measurements. The mild steel samples were also analyzed by Scanning Electron Microscopy (SEM). The results show that C1 is an excellent inhibitor for mild steel in acid medium. The inhibition was assumed to occur via adsorption of the inhibitor molecule on the metal surface. In the 298- 308 K temperature range, the C1, C2 and C3 adsorption follows Langmuir isotherm model. The protection efficiency increases with increasing the inhibitor concentration in the range of 250-1000 ppm but slightly decreases with increasing temperature.

Keywords: Mild Steel, Corrosion Inhibitors, Acid medium, Electrochemical impedance spectroscopy.

Introduction

Pure metal and alloys react chemically / electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal. The cathodic process requires the presence of an electron acceptor such

as oxygen or oxidizing agents or hydrogen ions¹⁻⁹. Corrosion can be minimized by suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reaction or both. Due to their environmental and acceptable ecological properties, naturally occurring antioxidants are cheap and readily available and renewable sources of materials¹⁰. These organic compounds are either synthesized or either extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. However, synergistic effects are often expected with these mixtures of inhibitors that may affect their inhibition efficiency. Several investigations have been reported using such economic plant extracts. El-Etre⁶ has studied the application of natural honey as corrosion inhibitor for copper in aqueous solution. Bouyanzer *et al.* studied Pennyroyal oil from menthe pulegium¹¹ as corrosion inhibition action for steel in acid media. Avwiri and coworkers studied the inhibitive action of *vernonia amygdaline*⁴ on the corrosion of aluminum alloys in HCl and HNO₃. *Nypa fruticans* wurmb² leaves were studied for the corrosion inhibition of mild steel in HCl media. *Lawsonia*¹ extract was studied for its inhibitive effect against acid induced corrosion of metals. El-Etre *et al* investigated khillah extract¹² for the corrosion inhibition of SS 316 steel in acid media. Oguzie studied the inhibitive effect of trifasciata¹³ extract on the acid and alkaline corrosion of aluminum alloy. P.C. Okafor *et al* *phyllanthus amarus*¹⁴ extracts for the corrosion inhibition of mild steel in acid media. Ethanolic extract of *Riccinus communis* leaves¹⁵ was studied for the corrosion inhibition of mild steel in acid media by sathanathan *et al.*

Hence in the present work, we have isolated three pyridine base alkaloids namely ricinine (**C1**), *N*-demethylricinine (**C2**) and 4-methoxy pyridine-3-carboxylic acid (**C3**) from methanolic extract of *Riccinus communis* leaves and investigated corrosion inhibition effect on mild steel in acidic medium using the weight loss and electrochemical techniques (Galvanostatic polarization and EIS).

Experimental

Ricinine (**C1**), *N*-demethylricinine (**C2**) and 4-methoxy pyridine-3-carboxylic acid (**C3**) was isolated from methanolic extract of *Riccinus communis* leaves by column chromatography method which was purified and analyzed by IR and ¹H NMR, ¹³C NMR and Mass spectra were scanned by effecting FAB spectroscopy techniques. The molecular structure of isolated compounds **a-c** is shown in Figure 1, which have been labeled **C1**, **C2** and **C3**. A 0.5 N HCl solution, prepared from an analytical reagent grade of HCl and distilled water, was used as corrosion media in this study. Corrosion tests were performed using coupons prepared from mild steel having the composition: 0.01 % C, 0.35 % Si, 0.018 % P, 0.04 % Cr, 0.03 % Mo, 0.017 % Ni, 0.02 % Cu 0.06 % Al and Fe balanced.

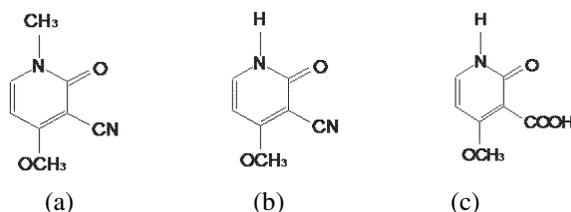


Figure 1. Chemical structure of the isolated compounds.

Electrochemical experiments were carried out in a conventional three-electrode cylindrical glass cell. Platinum and Saturated calomel electrodes (SCE) were used as counter

and reference electrode respectively. The working electrode (WE) was in the form of a disc of mild steel under investigation and was embedded in a talon rod with an exposed area of 0.5 cm^2 . The temperature is thermostatically controlled from 298 to 308 K. The polarization curves are recorded with a Keithley 220 programmable current source. The A.C impedance measurements were carried out in the frequency range from 42 Hz to 5 MHz using LCR Hi-Tester (H 10KI 3532-50). The charge transfer resistance (R_t) were obtained from Nyquist plots by determining the difference in the values of impedance at low and high frequencies as suggested by Tsuru and Haruyama¹⁶ and double-layer capacitance (C_{dl}) was calculated from the frequency at which the impedance imaginary component $-Z_{i_{\max}}$ is maximum using following equation:

$$C_{dl} = \frac{1}{2\pi f_{(-Z'_{\max})} R_t} \quad (1)$$

Inhibition efficiencies (%IE) were calculated as follows:

Galvanodynamic polarization measurement

$$\% P = \frac{I_{corr} - I_{corr}^0}{I_{corr}} \times 100 \quad (2)$$

Where, I_{corr} and I_{corr}^0 are the corrosion current densities in the absence and presence of the inhibitor.

Impedance measurements

$$\% P_{R_t} = \frac{R'_t - R_t}{R_t} \times 100 \quad (3)$$

Where, R_t and R'_t are the charge transfer resistance values without and with inhibitor respectively. The morphology of MS surface after and before treatment in test solutions was examined using Surface Electron Microscopy (SEM) (Jeol JSM 840). The corrosion products formed on steel surface during polarization were removed by scrapping and their FT-IR spectra were recorded. This study reveals the possibility of the adsorption on the inhibitor on the metal surface. FT-IR spectra (in KBr pellets) were recorded on a Hitachi-270.

Results and Discussion

Weight loss measurements

The weight loss of mild steel in 0.5 N HCl solutions with and without the addition of different concentrations of inhibitors was determined and compiled in Table 1.

It was observed from Table 1 that inhibition efficiency increases as the concentration of the inhibitor increases. This applies for all the three inhibitors. The maximum inhibition was obtained for the inhibitor concentration of 1000 ppm for each inhibitor at the testing temperatures. The inhibition efficiency decreases as the temperature increases. This behavior can be explained due to a reduction in the stability film of adsorbed film at higher temperatures; as temperature increases Gibbs free energy and enthalpy increases to a higher value, so that some of the chemical bonds joining the molecules onto the metallic are impaired and film stability reduced. The inhibition efficiency of these inhibitors tends to decrease in the following order:

$$C1 > C2 > C3$$

Table 1. Corrosion parameters obtained from weight loss measurements of various inhibitors taken at different concentrations and different temperatures in 0.5 N HCl.

| Inhibitor | Temp., K | Concentration, ppm | Weight Loss, g | IE, % |
|-----------|-------------|-----------------------|-------------------|----------|
| C1 | 298 | Blank | 0.5701 | -- |
| | | 250 | 0.1450 | 74.5 |
| | | 500 | 0.1385 | 75.7 |
| | | 1000 | 0.0698 | 87.7 |
| | 308 | Blank | 0.89 | -- |
| | | 250 | 0.34 | 61.7 |
| | | 500 | 0.23 | 74.1 |
| | | 1000 | 0.17 | 80.8 |
| C2 | 298 | Blank | 0.5701 | -- |
| | | 250 | 0.1745 | 69.39 |
| | | 500 | 0.1585 | 72.2 |
| | | 1000 | 0.0985 | 82.7 |
| | 308 | Blank | 0.89 | -- |
| | | 250 | 0.3645 | 59.04 |
| | | 500 | 0.26 | 70.78 |
| | | 1000 | 0.1954 | 78.04 |
| C3 | 298 | Blank | 0.5701 | -- |
| | | 250 | 0.1956 | 65.69 |
| | | 500 | 0.17 | 70.18 |
| | | 1000 | 0.1158 | 79.6 |
| | 308 | Blank | 0.89 | -- |
| | | 250 | 0.3894 | 56.24 |
| | | 500 | 0.2834 | 68.15 |
| | | 1000 | 0.2065 | 76.79 |

Electrochemical measurements

Figure 2 shows the polarization curves of mild steel in 0.5 N HCl solutions in the presence and absence of inhibitors respectively. Corrosion kinetic parameters were determined with and without inhibitors and summarized in Table 2. A decrease in both cathodic and anodic currents is noted. This result shows that the addition of inhibitors reduced anodic dissolution and also retards the hydrogen evolution reaction.

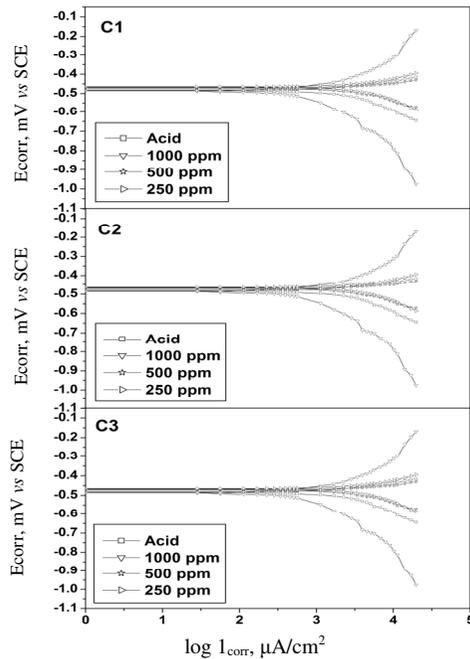


Figure 2. Galvanostatic polarization curve for different concentrations of inhibitors in 0.5 N HCl at 298 K.

Table 2. Corrosion parameters obtained from polarization measurements of various inhibitors taken at different concentrations and different temperatures in 0.5 N HCl.

| Inhibitor | Temp., K | Conc., ppm | E_{corr} , mV | I_{corr} , $\mu\text{A cm}^{-2}$ | θ | β_a , mV/dec | β_c , mV/dec | IE, % |
|-----------|----------|------------|-----------------|------------------------------------|----------|--------------------|--------------------|-------|
| C1 | 298 | Blank | 509 | 3.29 | -- | 87 | 167 | -- |
| | | 250 | 507 | 2.8 | 0.754 | 73 | 158 | 75.4 |
| | | 500 | 512 | 2.58 | 0.7673 | 65 | 153 | 76.73 |
| | | 1000 | 497 | 2.42 | 0.8687 | 57 | 145 | 86.87 |
| | | Blank | 502 | 3.33 | -- | 96 | 178 | -- |
| C2 | 308 | 250 | 504 | 2.91 | 0.6212 | 83 | 145 | 62.12 |
| | | 500 | 514 | 2.75 | 0.7374 | 72 | 125 | 73.74 |
| | | 1000 | 505 | 2.65 | 0.7943 | 68 | 112 | 79.43 |
| | | Blank | 509 | 3.29 | -- | 87 | 167 | -- |
| | | 250 | 500 | 2.84 | 0.6983 | 75 | 154 | 69.83 |
| C3 | 298 | 500 | 498 | 2.68 | 0.7264 | 61 | 151 | 72.64 |
| | | 1000 | 502 | 2.48 | 0.8229 | 54 | 148 | 82.29 |
| | | Blank | 502 | 3.33 | -- | 96 | 178 | -- |
| | | 250 | 504 | 2.93 | 0.6068 | 81 | 154 | 60.68 |
| | | 500 | 514 | 2.81 | 0.697 | 67 | 129 | 69.7 |
| C3 | 308 | 1000 | 505 | 2.67 | 0.7829 | 61 | 118 | 78.29 |
| | | Blank | 509 | 3.29 | -- | 87 | 167 | -- |
| | | 250 | 507 | 2.89 | 0.6583 | 76 | 155 | 65.83 |
| | | 500 | 512 | 2.71 | 0.713 | 61 | 152 | 71.3 |
| | | 1000 | 510 | 2.53 | 0.8069 | 59 | 147 | 80.69 |
| C3 | 308 | Blank | 502 | 3.33 | -- | 96 | 178 | -- |
| | | 250 | 504 | 2.96 | 0.571 | 78 | 158 | 57.1 |
| | | 500 | 514 | 2.82 | 0.6909 | 63 | 132 | 69.09 |
| | | 1000 | 505 | 2.69 | 0.7727 | 54 | 121 | 77.27 |

The corrosion behavior of mild steel, in acidic solution in the presence of inhibitors, was investigated by the EIS methods at 298K. Nyquist plots obtained for frequencies ranging from 42 Hz to 5 MHz at open circuit potential for mild steel in 1N HCl in the presence of various concentrations of inhibitors are shown in Figure 3. The values of charge transfer resistance R_t , double layer capacitance C_{dl} and inhibition efficiency for the corrosion of mild steel in 1 N HCl with different concentration of inhibitors are listed in Table 3. The presence of inhibitors enhances the values of R_t and reduces the C_{dl} may be due to the adsorption of inhibitors to form an adherent film on the metal surface and suggests that the coverage of the metal surface with this film increases the double layer thickness.

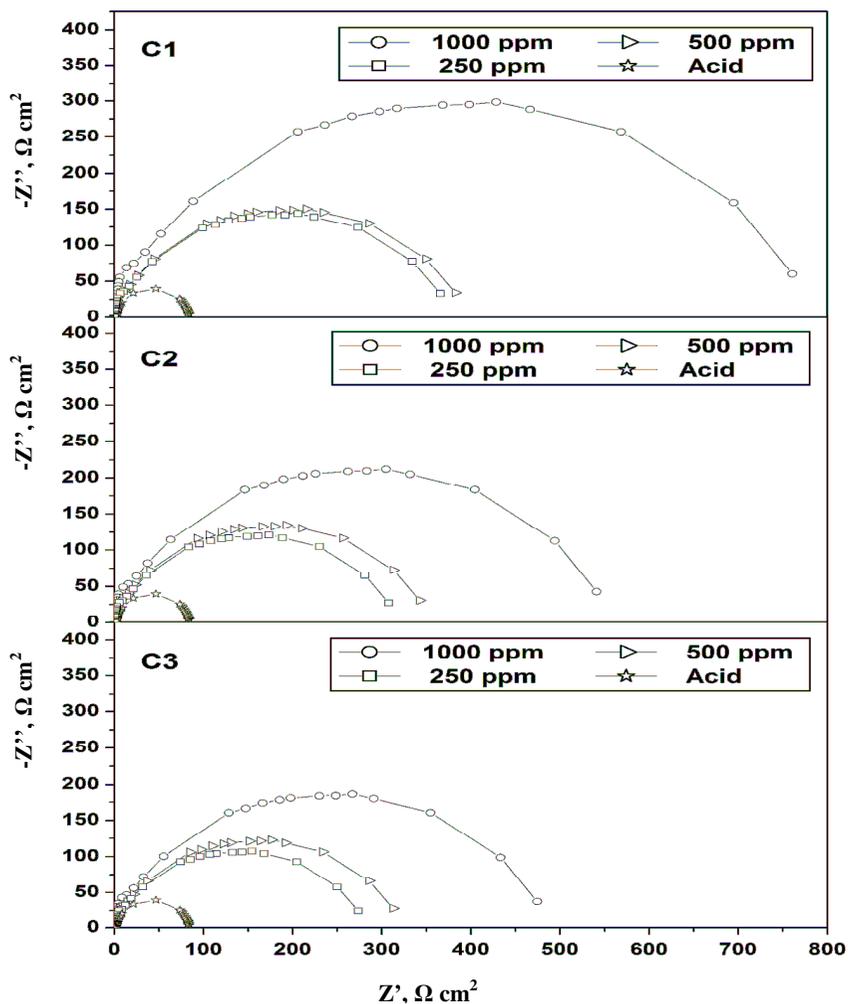


Figure 3. Nyquist plot for different concentrations of inhibitors in 0.5 N HCl.

Adsorption isotherm

The activation parameters for the corrosion process were calculated from Arrhenius type plot according to the following equation:

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

and from transition state plot according to the following equation:

$$\frac{\theta}{1-\theta} = AC \exp\left(-\frac{\Delta H}{RT}\right) \quad (5)$$

Where, E_a is the apparent activation energy, R the universal gas constant, ΔH the enthalpy of activation and T the absolute temperature. The variations of logarithm of the corrosion rate of mild steel reciprocal of the absolute temperature are presented in Figure 4 and Figure 5. The E_a and ΔH values were determined from the slopes of these plots. The calculated values of E_a and ΔH in the absence and presence of inhibitors are given in Table 3.

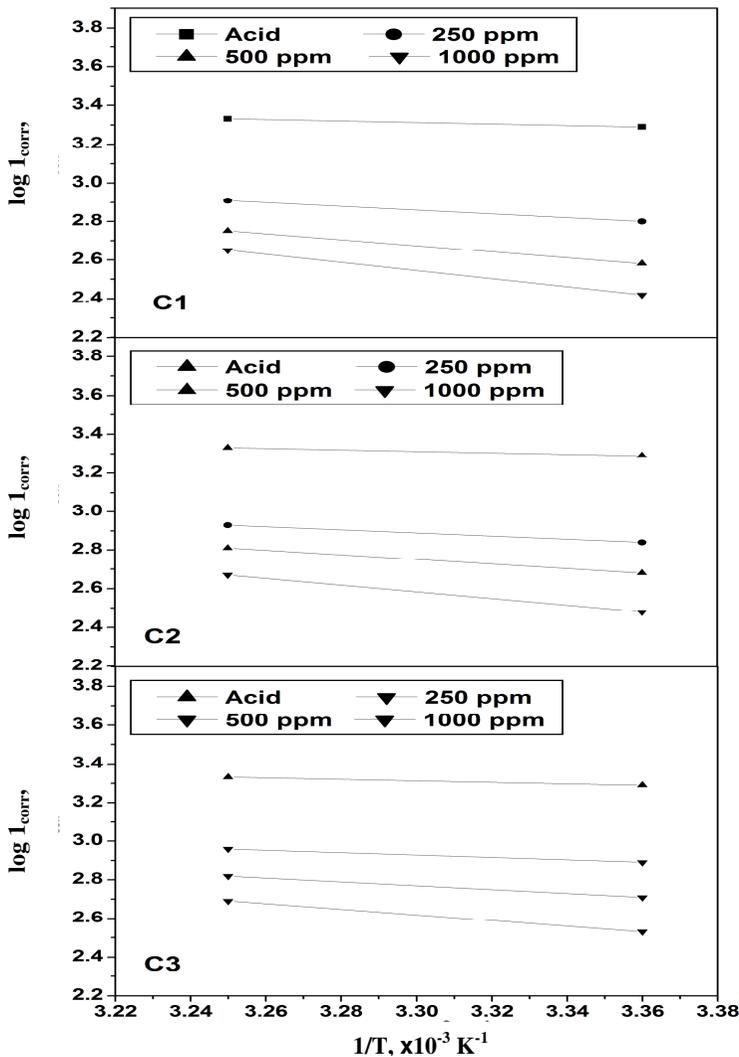


Figure 4. Variation of corrosion current with temperature at different concentration of inhibitors in 0.5 N HCl.

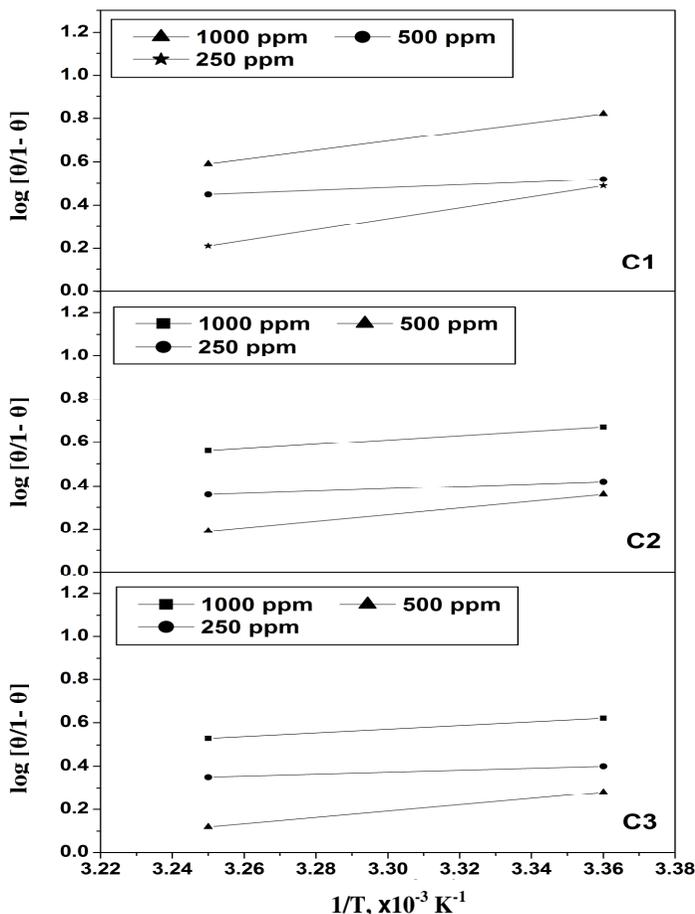


Figure 5. Arrhenius plots $\log [\theta / (1-\theta)]$ vs. $1/T$ in 0.5 N HCl at various concentrations of inhibitors.

Table 3. Electrochemical, thermodynamic parameters and inhibition efficiency obtained for mild steel in 0.5 N HCl with different concentrations of inhibitors at 298 K.

| Inhibitor | Conc., ppm | R_p , Ωcm^2 | Capacitance, $\mu\text{F cm}^2$ | E_a , kJ mol^{-1} | ΔH , kJ mol^{-1} | IE, % |
|-----------|------------|-----------------------------|---------------------------------|------------------------------|-----------------------------------|-------|
| C1 | Blank | 91 | 345 | 7.02 | -- | -- |
| | 250 | 359 | 163 | 19.31 | -- | 74.7 |
| | 500 | 376 | 156 | 29.84 | -- | 75.8 |
| | 1000 | 746 | 78.5 | 40.37 | 41.1 | 87.8 |
| C2 | Blank | 91 | 345 | 7.02 | -- | -- |
| | 250 | 302 | 194 | 15.8 | -- | 69.8 |
| | 500 | 337 | 174 | 22.82 | -- | 73.0 |
| | 1000 | 530 | 110 | 33.35 | 19.35 | 82.8 |
| C3 | Blank | 91 | 345 | 7.02 | -- | -- |
| | 250 | 269 | 218 | 12.29 | -- | 66.2 |
| | 500 | 307 | 190 | 19.31 | -- | 70.3 |
| | 1000 | 465 | 125 | 28.08 | 15.75 | 80.4 |

This result agrees with the order of IE. The activation energy is higher in the presence of additives than in its absence. During the corrosion reaction mechanism, the charge transfer is blocked with adsorption of inhibitor molecules to the metal surface, causing the increase in the activation energy¹⁷. The higher values of E_a are good evidence for the chemisorptions mechanism on the mild steel surface. The negative values of ΔH reflect the exothermic behavior of inhibitors on the metal surface.

The increase in the inhibition efficiencies of mild steel, in 1N acid chloride solution, with increasing additive concentration can be explained on the basis of additive adsorption. In the present medium, the additives were seen to follow the Langmuir adsorption isotherm as seen in Figure 6.

$$KC = \frac{\theta}{1-\theta} \tag{6}$$

Where, θ is the degree of surface coverage, K the equilibrium constant and C is additive concentration.

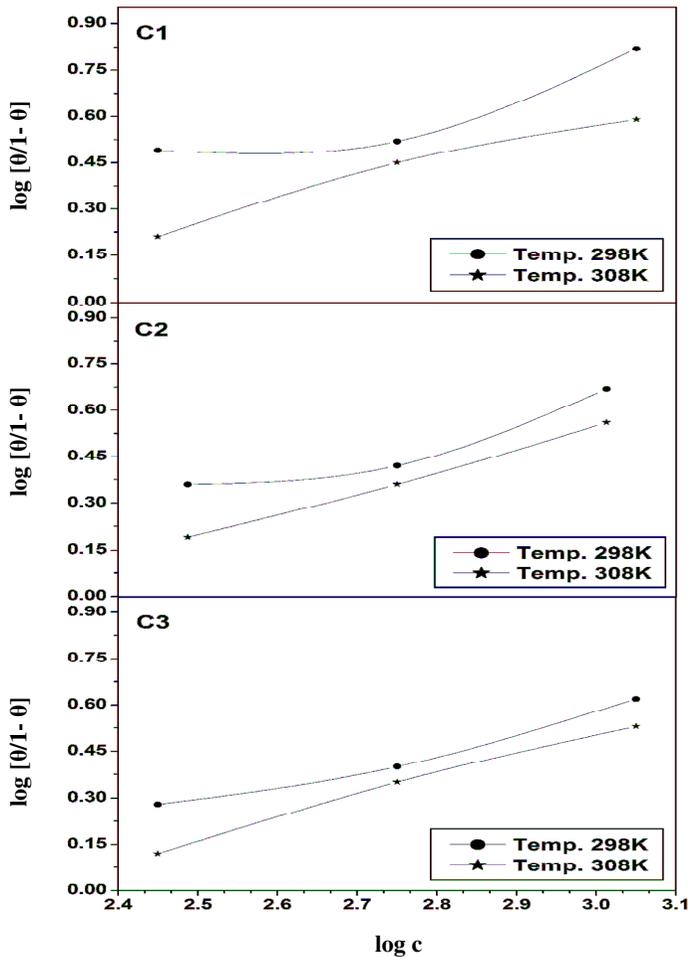


Figure 6. Langmuir adsorption isotherm at different temperatures for different inhibitors in 0.5 N HCl.

Morphological investigation

Microstructural studies of mild steel in 0.5 N HCl in absence and presence of a certain concentration of C1 compound at 298K were performed and illustrated in Figure 7a & 7b. It is clear that the corrosion attack was more pronounced in the absence of inhibitor at 298K temperature (Figure 7a), while the film formed on the metal surface becomes more protective with increase in inhibitor concentration (1000 ppm) at 298K (Figure 7b). This is attributed to the involvement of C1 compound in the interaction with the active sites of metal surface. This results in enhanced surface coverage of the metal so that there is a contact between metal and the aggressive medium.

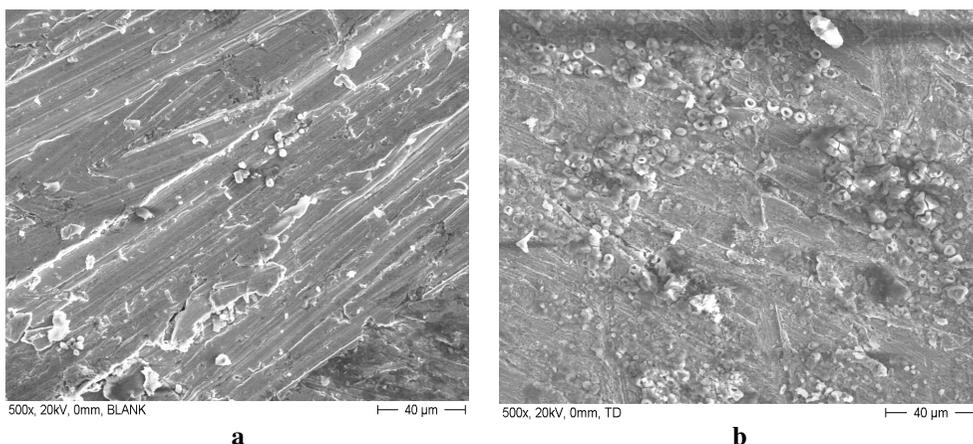


Figure 7- SEM image of mild steel (a) in 0.5N HCl medium, (b) with C1 inhibitor (1000ppm).

FTIR studies

The compounds, formed on the corroded mild steel specimens after polarization, were scrapped, collected and subjected to FT-IR spectral studies. The involvement of OCH₃ group, C-H str, N-H (bend) and C-O alcoholic in interaction reaction with metal surface atom could be proved by the respective IR spectra. The shift in the adsorption peaks from OCH₃ (3113-3105), C-H str. (2998-2990), N-H (1616-1600) and C-O alcoholic (1099-1081), further the intensity of the peaks stretching frequency is decreased which implies that the shift peaks in this compound is coordinated to Fe⁺² resulting in the formation of a Fe⁺² inhibitor complex on the metal surface.

Conclusion

- a. The inhibition efficiency of designed molecules increases by increasing the inhibitor concentration, but it decreases with increase in the testing temperature. The order of inhibition efficiency was correlated with the modification of the molecular structure of inhibitors, while the decrease in inhibitor efficiency with temperature was ascribed to the thermodynamic parameters due changes in the nature of molecular interactions.
- b. The galvanostatic polarization curves indicate that ricinine (C1), *N*-demethylricinine (C2) and 4-methoxy pyridinine-3-carboxylic acid-2-one (C3) inhibit both anodic metal dissolution and cathodic hydrogen evolution reaction. These are mixed type inhibitors.

- c. All the pyridine base alkaloids perform well as corrosion inhibitors in hydrochloric acid solution and the inhibiting efficiencies follow the order ricinine (**C1**) > *N*- demethylricinine (**C2**) > 4-methoxy pyridinine-3-carboxylic acid-2one (**C3**).
- d. Impedance measurements at the corrosion potential showed a single capacitive loop.
- e. Both Polarization and AC impedance measurements show that the inhibition efficiency has increased with increasing inhibitor concentration.
- f. The adsorption of **C1**, **C2** and **C3** molecules on the metal surface in 0.5 N HCl solutions obeys Langmuir adsorption isotherm. The negative sign of the ΔH indicate that the adsorption process is spontaneous and exothermic.
- g. The analysis of the SEM images suggests that the corrosion of the mild steel is mainly through pitting and the addition of inhibitor in the aggressive solution results in the formation of the protective film on mild steel surface.

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