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## Electrochemical behavior for corrosion protection of mild steel (MS) in 1M HCl medium by using lidocaine drug as an inhibitor

### ABSTRACT

*The impact of Lidocaine as a save corrosion inhibitor for mild steel (MS) in 1M HCl by using weight loss (WL), Hydrogen evaluation (HE), open circuit potential ( $E_{ocp}$ ), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) and Electrochemical frequency modulation (EFM) techniques has been investigated. Weight loss studied at various temperatures between (25– 45°C) but Hydrogen evaluation and electrochemical studies at room temperature. The effect of temperature on the inhibition of corrosion has been studied and the thermodynamic activation and adsorption parameters were calculated. The morphology of MS was examined by scanning electron microscope with energy dispersive X-ray spectroscopy (SEM–EDX) technology and atomic force microscopy (AFM). EIS data indicate that in the presence of drug the double layer capacitance was decreased and the charge transfer resistance increased. The adsorption of the Lidocaine on MS surface was found to obey Langmuir adsorption isotherm and elucidate the mechanism of corrosion inhibition. The Lidocaine drug acts as mixed type inhibitor. All surface examination confirms the formation thin film covered the surface of the metal and prevent the surface of the metal from corrosion.*

**Keywords:** Adsorption; inhibition; electrochemical techniques; SEM; EDX; AFM.

### 1. INTRODUCTION

Corrosion is a principal process and considered as an important role in economics and safety, especially for metals [1]. The utilization of inhibitors is one of the most methods for protection against corrosion especially in acidic media [2-4]. Most well-known acid inhibitors are organic compounds containing nitrogen (N-heterocyclic), sulfur, long carbon chain or aromatic and oxygen atoms. Among them, organic inhibitors have many advantages such as high inhibition efficiency, low price, low toxicity, and easy production [5-7]. Organic heterocyclic compounds have been used for the corrosion inhibition of carbon steel [8-13], copper [14,15], aluminum [16-18], and other metals

[19] in different aqueous media. Many drugs are facilitated the adsorption on the metal surface [20-22], Such as ampiclox, ampicillin, tetracycline, cloxacillin, azithromycin and orphenadrine have been discovered as great inhibitors for corrosion of metals. The select of some medication for corrosion inhibitors are taking in the following: 1) drug molecules contain oxygen, sulphur and nitrogen as active sites, 2) it is reportedly environmentally friendly furthermore vital in organic responses and 3) drugs can be easily produced and purified [23-27]. Heterocyclic compounds have shown a high inhibition efficiency for carbon steel in both HCl [28] and H<sub>2</sub>SO<sub>4</sub> [29] solutions. The following Table 1 contains some drugs gives an inhibition efficiency in aqueous medium.

The scope of this paper is to use Lidocaine drug as save corrosion inhibitor for mild steel in acid medium by various chemical and electrochemical methods, and to elucidate the mechanism of corrosion inhibition.

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Table 1. %IE of some drugs in acidic media and for different metal

Tabela 1. % IE nekih lekova u kiselim medijima za različite metale

| Inhibitor (Drug)                                | Sample   | Medium                             | IE % | References |
|---|----------|------------------------------------|------|------------|
| Lidocaine                                       | C-steel  | 1M HCl                             | 76,9 | This work  |
| Biopolymer                                      | Copper   | NaCl                               | 86.0 | [30]       |
| pyromellitic diimide linked to oxadiazole cycle | C-steel  | 0.3M HCl                           | 84.9 | [31]       |
| 2-mercaptobenzimidazole                         | C-steel  | 1M HCl                             | 82.0 | [32]       |
| Antidiabetic Drug Janumet                       | MS       | 1M HCl                             | 88.7 | [33]       |
| Januvia   | Zinc     | 0.1-2.5 M HCl                      | 79.5 | [34]       |
| Cefuroxime Axetil                               | Aluminum | 0.5 M HCl                          | 89.9 | [35]       |
| Phenytoin sodium                                | C-steel  | 1MHCl                              | 79.0 | [36]       |
| Aspirin   | MS       | 0.5MH <sub>2</sub> SO <sub>4</sub> | 71.0 | [37]       |
| Septazole                                       | Copper   | 0.1M HCl                           | 84.8 | [38]       |
| Chloroquine diphosphate                         | MS       | 0.1M HCl                           | 80.0 | [39]       |

## 2. EXPERIMENTAL DETAIL

### 2.1. Metal sample

The composition of metal sample (MS) is:

Chemical composition (wt %) of the MS: C 0.10, Mn 0.40, P 0.06, S 0.026 and rest Fe

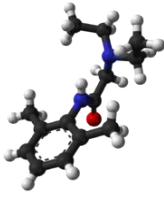
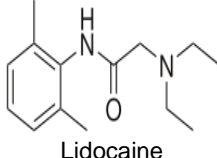
### 2.2. Chemicals

#### 2.2.1. Inhibitor

Lidocaine drug is an inhibitor which describing in Table 2. The pharmaceutical drug has been investigated and purchased from Sandozinc and Pfizer inc companies.

Table 2. The Component and molecular structure of the investigated inhibitor

Tabela 2. Komponente i molekularna struktura istraženog inhibitora

| Chemical formula                                 | Active center     | Molecular weight | IUPAC Name                                      | Structure  |   | Drug      |
|--|-------------------|------------------|---|--|---|-----------|
| C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O | O<br>2N<br>π bond | 234.34 g/mol     | N-(2,6-dimethylphenyl)-N',N'-diethylglycinamide |  |  | Lidocaine |

#### 2.2.2. Solutions

The aggressive solution, 1M HCl was prepared by dilution of analytical grade (% 37) HCl with bidistill water. The concentration range of the Lidocaine that used between (50 and 300 ppm).

### 2.3. Methods used for corrosion techniques

#### 2.3.1. Weight loss technique (WL)

Collection data of WL by using seven square specimens having surface area (2 cm x 2 cm) x 2mm, which exposed to the corrosive medium under study. The metal samples were abraded by polisher papers (SiC) have deferent sizes like (400,800 and 1200), washed with acetone. Then rinsed several times with bidistilled water, and finally dried by filter paper. Collection data of WL were occurred or carried out in 100 ml glass beaker

that placed in thermostat or water bath. The metal samples submersed soon in corrosive medium in nonexistence and existence various doses of Lidocaine drug.

All aggressive acid solutions were opened to air. During three hours, the specimens were taken out, washed, dried, and weighed accurately per thirty minutes. The average weight loss for seven square MS specimens can be obtained.

The inhibition efficiency (% IE) and the degree of surface coverage (θ) were calculated as follows [40]:

$$\% IE = \theta \times 100 = [1 - (W/W^0)] \times 100 \quad (1)$$

where, W<sup>0</sup> and W are the weight losses, without and with adding deferent doses of investigated inhibitor respectively.

### 2.3.2. Gasometric measurements

Measurements of hydrogen evolutions were estimated at 25°C, and the hydrogen volume developed every 15 minutes.  $k$  values can be calculated from the slope according to equation (2). The degree of surface coverage ( $\Theta$ ) and the efficiency of inhibition (% IE) were calculated by (3) and (4).

$$V = k t \quad (2)$$

where,  $V$  is the volume of hydrogen in  $\text{cm}^3$ ,  $k$  is rate constant and  $t$  is time in minute.

$$\Theta = 1 - k/k^0 \quad (3)$$

where,  $k^0$  and  $k$  are the rate constant of corrosion in absence and presence inhibitor, which calculated by plotting  $V$  vs.  $t$  gives straight line

$$\% \text{ IE} = \Theta \times 100 \quad (4)$$

### 2.3.3. Potentiodynamic polarization (PP) technique

Electrochemical polarization experiments using three electrodes in electrochemical cell such as saturated calomel electrode (SCE) that couple to a fine Luggin capillary act a reference electrode, platinum foil is counter electrode and working electrode that made up from square cut of metal (MS) sheet fixed in epoxy resin so that the surface area that exposed to the electrolyte  $1.0 \text{ cm}^2$  only. The working electrode prepared by polisher paper (SiC) with deferent sizes (800, 1000 and 1200) and immersed in corrosive medium at natural potential for 10 min until reach the steady state.

The potential was started from - 500 to + 500 mV vs. open circuit potential ( $E_{\text{ocp}}$ ). Calculation of inhibition efficiency (% IE) and the degree of surface coverage ( $\Theta$ ) are as follows [41]:

$$\text{IE \%} = \Theta \times 100 = [1 - (i_{\text{corr(inh)}} / i_{\text{corr(free)}})] \times 100 \quad (5)$$

where,  $i_{\text{corr(free)}}$  and  $i_{\text{corr(inh)}}$  are the corrosion current densities in the absence and presence of Lidocaine, respectively.

### 2.3.4. Electrochemical Impedance Spectroscopy (EIS) technique

The measurements of EIS were achieved at  $25 \pm 1^\circ\text{C}$  over a wide frequency range of ( $1 \times 10^5 \text{ Hz}$  to  $\times 0.1 \text{ Hz}$ ). The potential perturbation was 10 mV in amplitude peak to peak. The obtained diameters of the capacitive loops increase in the presence of inhibitor and decrease the capacitance double layer ( $C_{\text{dl}}$ ) which defined as equation (7):

The inhibition efficiency (% IE) and the surface coverage ( $\Theta$ ) obtained from the impedance measurements were calculated by the following relation:

$$\text{IE \%} = \Theta \times 100 = [1 - (R_p^0 / R_p)] \times 100 \quad (6)$$

where,  $R_p^0$  and  $R_p$  are the charge transfer resistances in the absence and presence of inhibitor, respectively. The double layer capacitance was calculated using equation (7)

$$C_{\text{dl}} = 1 / (2 \pi f_{\text{max}} R_p) \quad (7)$$

where,  $f_{\text{max}}$  is the maximum frequency.

### 2.3.5. Electrochemical Frequency Modulation (EFM) technique

The measurements of EFM were achieved by using potential perturbation signal have abundance 10 mV with two sine waves of 2 and 5 Hz that based on three factors:

1. Large peaks were used to calculate the corrosion current density ( $i_{\text{corr}}$ )
2. Tafel slopes ( $\beta_c$  &  $\beta_a$ )
3. Causality factors ( $\text{CF}_2$  &  $\text{CF}_3$ ) [42,43].

The inhibition efficiency ( $\% \text{IE}_{\text{EFM}}$ ) was calculated as follows:

$$\% \text{ IE}_{\text{EFM}} = [1 - (i_{\text{corr}}^0 / i_{\text{corr}}^p)] \times 100 \quad (8)$$

where,  $i_{\text{corr}}^0$  and  $i_{\text{corr}}^p$  are corrosion current densities in the absence and presence of inhibitor, respectively.

All electrochemical techniques achieved by using Gamry instrument PCI300/4 Potentiostat/ Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 Electrochemical Impedance Spectroscopy software, EFM140 Electrochemical Frequency Modulation software and Echem Analyst the results plotting, graphing, data fitting and calculating.

### 2. 3.6. Surface Examinations

The morphology of the MS surface used for analysis and examination nature of the surface and study the changing that appeared on the metal surface. The specimens were prepared by abraded mechanically by using different emery papers up to 1200 grit size and immersed in 1M HCl acid (blank) and with 300 ppm of Lidocaine at room temperature for one day (24 h). Then, after this immersion time, the specimens were washed gently with bidistilled water, carefully dried and take carefully to the system of surface examinations such as scanning electron microscope (SEM), energy dispersive x-ray (EDX) and atomic force microscope (AFM).

## 3. RESULTS AND DISCUSSION

### 3.1. Weight loss measurement (WL)

WL of MS in  $\text{mg cm}^{-2}$  of the metal surface that detected at different times in nonexistence and existence of various doses (50 – 300 ppm) of the

Lidocaine drug. The bending line or curves obtained in the existence of various doses of Lidocaine falls down the comparing with in free acid that seen in Fig. 1. The efficiency (% IE) are listed in Table 3. In all cases, the efficiency of the

drug increases with increasing doses of drug but the rate of corrosion were decreased. These results indicated that, the Lidocaine under investigation are good efficient as inhibitor for MS that prevent dissolution in corrosive medium.

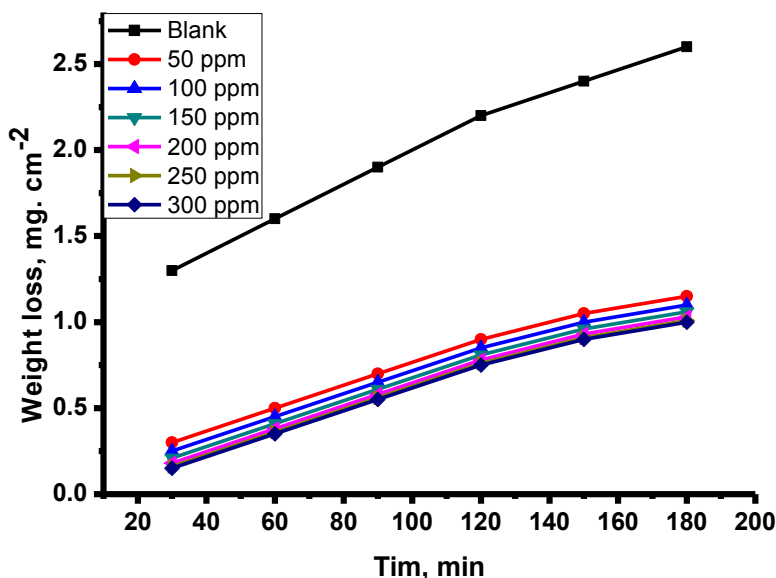


Figure 1 Weight loss-time curves for the dissolution of MS in the nonexistence and existence of various doses of Lidocaine at 25°C

Slika 1. Krive gubitak težine - vreme rastvaranja MS u prisustvu i odsustvu različitih doza leka Lidokaina na 25°C

Table 3. Variation of inhibition efficiency (% IE) of Lidocaine with their doses at 25°C from WL measurements at 120 min submersion in 1M HCl

Tabela 3. Promena efikasnosti inhibicije (% IE) Lidokaina pri različitim koncentracijama na 25°C merenjem VL pri potapanju od 120 minuta u 1M HCl

| % IE | $k_{corr} \times 10^{-3}$<br>mg cm <sup>-2</sup> min <sup>-1</sup> | Conc.<br>ppm | Compound  |
|------|--|--------------|-----------|
| ---- | 18.0   | ---          | Blank     |
| 59.1 | 8.0  | 50           | Lidocaine |
| 61.4 | 7.9  | 100          |           |
| 63.2 | 7.5  | 150          |           |
| 64.6 | 7.1  | 200          |           |
| 65.5 | 6.9  | 250          |           |
| 65.9 | 6.5  | 300          |           |

### 3.1.1. Effect of temperature

The rate of corrosion or the rate constant ( $k_{corr}$ ) are expressed by Arrhenius equation as follows:

$$\log k_{corr} = \log A - (E_a^*/2.303RT) \quad (9)$$

where, R is general gas law constant, T is absolute temperature,  $E_a^*$  is the activation energy and A is Arrhenius pre-exponential constant or frequency factor that depends on the type of metal and the nature of the electrolyte. Plot  $k_{corr}$  vs. (1/T) according Arrhenius equation (9) for MS in 1M HCl in the nonexistence and existence various doses of Lidocaine drug is seen diagrammatically in Fig. 2. The variation of  $\log k_{corr}$  vs. (1/T) is a linear one and the values of  $E_a^*$  that obtained and recorded in Table 4. From the results, data in the table express the Lidocaine exhibit the similar mechanism action. It obvious that the  $E_a^*$  increases with increasing various doses of Lidocaine drug indicating that, the energy barrier for the corrosion reaction increased [44].

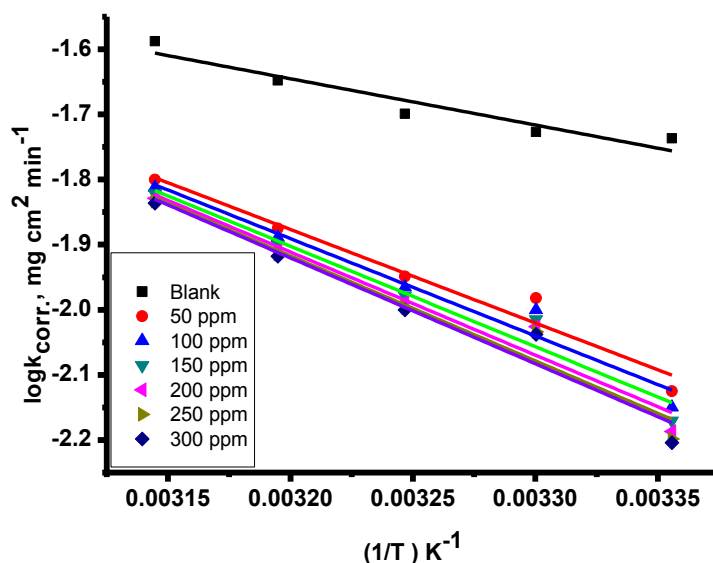


Figure 2 Arrhenius plots ( $\log k_{\text{corr}}$  vs.  $1/T$ ) for corrosion of MS in 1M HCl in the nonexistence and existence of various doses of Lidocaine drug

Slika 2. Arrhenius-ove krive ( $\log k_{\text{corr}}$  vs.  $1/T$ ) za koroziju MS u 1M HCl u prisustvu i odsustvu različitih doza leka Lidokain

The activation parameter like enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) are calculated by using transition state theory equation (10) [45]:

$$k_{\text{corr}} = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (10)$$

where,  $N$  is Avogadro's number and  $h$  is Planck's constant. Plotting  $\log(k_{\text{corr}}/T)$  vs.  $(1/T)$  according to the above equation (10) either gives straight lines that seen in Fig. 3, for MS that dissolution in 1M HCl in nonexistence and with existence various doses of Lidocaine drug. The inclines or slope of straight lines equal  $-\Delta H^*/2.303R$  and the intercept equal  $[\log(RT/Nh) + (\Delta S^*/2.303R)]$ , from slope and intercept the activation parameter will be calculated ( $\Delta H^*$  and  $\Delta S^*$ ) and listed in Table 4. From these results, it is obvious that in the existence of the Lidocaine drug increases the  $E_a^*$  values and on the other hand diminishes the corrosion rate of the MS. Lidocaine acted as inhibitor according to increase in  $E_a^*$  values and diminishes the dissolution of MS by made up energy barrier and mass that prevents the charge transfer due to the adsorption of the drug on the MS surface. The enthalpy values refer to strength of adsorption on metal surface. The enthalpy of  $\Delta S^*$  in nonexistence and with existence of the Lidocaine drug is large and negative, this means the activated complex in the rate-determining step prefer an association rather than

dissociation step, indicating that a decrease in randomness that takes place i.e. the reactants going to the activated complex and the activated molecules were placed more ordered than that the initial state [46].

Table 4. Thermodynamic activation parameters for the dissolution of MS in 1M HCl in the nonexistence and existence of various doses of Lidocaine drug

Tabela 4. Termodinamički parametri aktivacije rastvaranja MS u 1M HCl u prisustvu i odsustvu različitih doza leka Lidokain

| Conc.<br>Ppm | Activation parameters           |                                      |  |
|--------------|---------------------------------|--------------------------------------|--|
|              | $E_a^*$<br>$\text{kJ mol}^{-1}$ | $\Delta H^*$<br>$\text{kJ mol}^{-1}$ | $-\Delta S^*$<br>$\text{J mol}^{-1} \text{K}^{-1}$ |
| Blank        | 13.59                           | 11.1                                 | 241.43   |
| 50           | 2.74                            | 2.5                                  | 201.41   |
| 100          | 2.85                            | 2.6                                  | 198.16   |
| 150          | 2.95                            | 2.7                                  | 195.48   |
| 200          | 3.03                            | 2.8                                  | 193.18   |
| 250          | 3.08                            | 2.8                                  | 241.43   |
| 300          | 3.10                            | 2.9                                  | 201.41   |

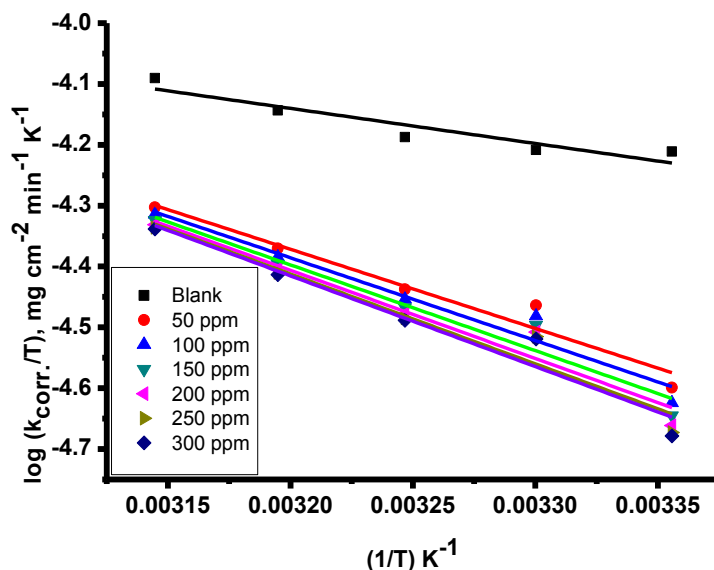


Figure 3. Plots of  $(\log k_{\text{corr.}} / T)$  vs.  $(1/T)$  for corrosion of MS in 1M HCl in the nonexistence and existence of various doses of Lidocaine drug

Slika 3. Krive  $(\log k_{\text{corr.}} / T)$  vs.  $(1/T)$  za koroziju MS u 1M HCl u prisustvu i odsustvu različitih doza leka Lidokain

### 3.1.2. Adsorption isotherms

Assuming that the corrosion inhibition is due to the adsorption of Lidocaine and the values of  $\theta$  for various doses of Lidocaine in 1M HCl were detected from WL measurement by using equation (1):

The values of  $(\theta)$  increased with increasing the doses of Lidocaine. Using these values of  $(\theta)$  and applying in different adsorption isotherms to obey

with experimental data. Langmuir adsorption isotherm was found and gives fit experimental data. The mathematical expression of Langmuir is given as follows equation [47]:

$$C/\theta = 1/K_{\text{ads.}} + C \quad (11)$$

where,  $K_{\text{ads.}}$  is the adsorption equilibrium constant and  $C$  is concentration of Lidocaine drug.

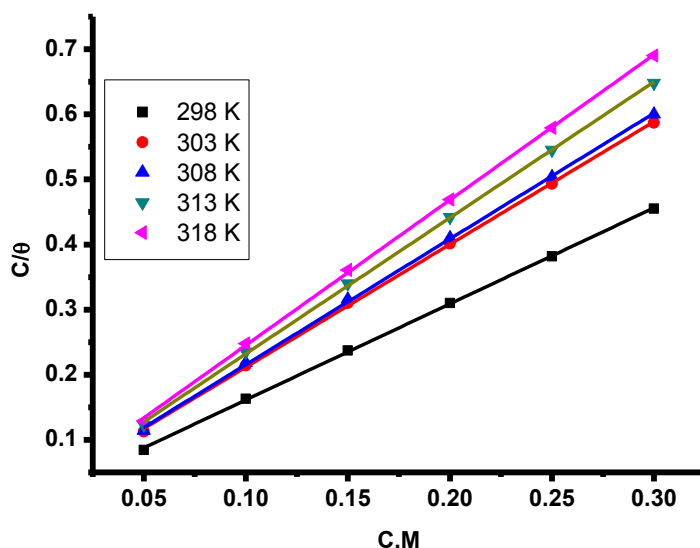


Figure 4. Langmuir adsorption isotherm plotted as  $(\log C/\theta \text{ vs. } C, M)$  of the investigated inhibitor for corrosion of MS in 1M HCl solution from weight loss method at 25°C

Slika 4. Langmuir-ova adsorpciona izoterma  $(\log C/\theta \text{ vs. } C, M)$  ispitivanih inhibitora za koroziju MS u 1M HCl metodom gubitaka težine na 25°C



Plotting  $(C/\theta)$  versus  $(C)$  of Lidocaine at various temperatures is introduced in Fig. 4. Linearly relationship are given with intercept equal to  $(1/K_{ads.})$  and slope similar the unity, the adsorption constant being result to the standard free energy of  $\Delta G_{ads.}^{\circ}$  adsorption by the relation:

$$\Delta G_{ads.}^{\circ} = -RT \ln (55.5 K_{ads.}) \quad (12)$$

where,  $R$  is the universal gas constant,  $T$  is the absolute temperature and 55.5 is the concentration of water in the solution in M/L. The  $\Delta G_{ads.}^{\circ}$  values at all studied temperatures, which calculated by above equation (12) and recorded in Table 5.

The heat of adsorption ( $\Delta H_{ads.}^{\circ}$ ) was calculated according to the Van't Hoff equation [48].

$$\log K_{ads.} = (-\Delta H_{ads.}^{\circ} / 2.303RT) + \text{constant} \quad (13)$$

Plotting  $(K_{ads.})$  against  $(1/T)$  give straight line that shown in Fig. 5, the straight line gives slope equal  $(\Delta H_{ads.}^{\circ} / 2.303R)$ , from this slope, the  $\Delta H_{ads.}^{\circ}$  were calculated and is listing in Table 5.

$$\Delta G_{ads.}^{\circ} = \Delta H_{ads.}^{\circ} - T\Delta S_{ads.}^{\circ} \quad (14)$$

Table 5. Equilibrium constant ( $K_{ads.}$ ), adsorption free energy ( $\Delta G_{ads.}^{\circ}$ ) for the adsorption of inhibitor on MS in 1M HCl from weight loss method at 25°C.

Tabela 5. Konstanta ravnoteže ( $K_{ads.}$ ), bez adsorpcije energije ( $\Delta G_{ads.}^{\circ}$ ) za adsorpciju inhibitora na MS u 1M HCl metodom gubitaka težine na 25°C.

| Temp. °C | $K_{ads.} M^{-1}$ | $-\Delta G_{ads.}^{\circ} kJ mol^{-1}$ | $\Delta H_{ads.}^{\circ} kJ mol^{-1}$ | $\Delta S_{ads.}^{\circ} J mol^{-1} K^{-1}$ |
|----------|-------------------|--|---------------------------------------|---|
| 25       | 72.8              | 20.6                                   | 9.9                                   | 102.3                                       |
| 30       | 43.6              | 19.6                                   |                                       | 97.5  |
| 35       | 44.8              | 20.0                                   |                                       | 97.2  |
| 40       | 43.2              | 20.3                                   |                                       | 96.4  |
| 45       | 45.3              | 20.7                                   |                                       | 96.2  |

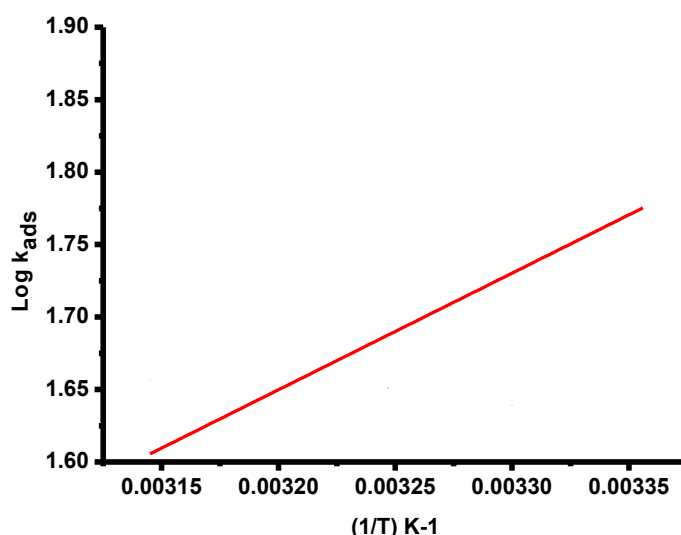


Figure 5. Plot ( $\log K_{ads.}$ ) vs  $(1/T)$  for the corrosion of MS in 1M HCl in the presence of Lidocaine at different temperatures.

Slika 5. Kriva ( $\log k_{ads.}$ ) vs  $(1/T)$  za koroziju MS u 1M HCl u prisustvu Lidokaina na različitim temperaturama

From introducing the values of  $\Delta G_{ads.}^{\circ}$  and  $\Delta H_{ads.}^{\circ}$ , the  $\Delta S_{ads.}^{\circ}$  was calculated at all studied temperatures by the above equation (14). All thermodynamic adsorption parameters for Lidocaine inhibitor on MS from 1M HCl solution can be concluded that:

1. The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients were in the range (0.99 - 0.98).

- $K_{ads.}$  values increases with increasing temperatures from 30 to 45°C except at 25°C.
- The negative values of  $\Delta G_{ads.}^{\circ}$  reflected that the adsorption of Lidocaine on MS surface in 1 M HCl solution is spontaneous process.
- The value of  $\Delta G_{ads.}^{\circ}$  slightly less than  $-20 kJ mol^{-1}$  indicate that the electrostatic attraction between charged metal surface and charge organic

molecules in the bulk of the solution i.e. mixed type physical and chemical adsorption[49].

5. The positive sign of  $\Delta H_{\text{ads}}^{\circ}$  refer to the adsorption of drug molecules is an endothermic process, indicate that the adsorption is chemisorption. The unshared electron pairs in investigate molecule may attractive with positive center and or the vacant orbital on the surface of MS by electrostatic attraction to produce a protective film prevent corrosion process [50].
6. The values of  $\Delta S_{\text{ads}}^{\circ}$  in the presence of investigate inhibitor are positive and decreases with increasing doses of inhibitor this means that the adsorption is more ordered with increasing temperatures and enhances the chemisorption [51].

### 3.2. Hydrogen Evaluation (HE)

All information draws from the volume of hydrogen, which produces at versus time, in presence of Lidocaine doses (from 50 to 300 ppm) in Fig. 6. The slope of line evaluated the rate of corrosion. The great straight lines show the insoluble film on the metal surface. The certain of the rate of corrosion acquired from hydrogen evaluation individually at versus doses are recorded in Table 6. It is clear that, the rate of corrosion reduced with increasing of Lidocaine dose, appearing diminishes conduct for the metal

disintegration. This result is normal on the grounds that with increasing drug, both acidity and  $\text{Cl}^-$  ion focus are lessening, according to the chemical equation (15) pointed out that Fe dissociation in acid arrangements relies on hydrogen ion more than the chloride ion [52].  $\text{H}^+$  advancement and mass misfortune is delivered by the same response:

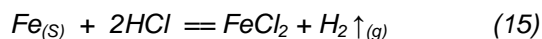


Table 6. The rate of corrosion for MS at existence of various doses of Lidocaine drug

Tabela 6. Stepen koroziije za metal pri prisustvu različitih doza leka Lidokain

| Conc. ppm | $k_{\text{corr}}$<br>$\text{ml cm}^{-2} \text{ min}^{-1}$ | $\theta$ | % IE  |
|-----------|---|----------|-------|
| Blank     | 0.165   | -----    | ----- |
| 50        | 0.055   | 0.667    | 66.7  |
| 100       | 0.051   | 0.691    | 69.1  |
| 150       | 0.049   | 0.703    | 70.3  |
| 200       | 0.046   | 0.721    | 72.1  |
| 250       | 0.043   | 0.739    | 73.9  |
| 300       | 0.038   | 0.769    | 76.9  |

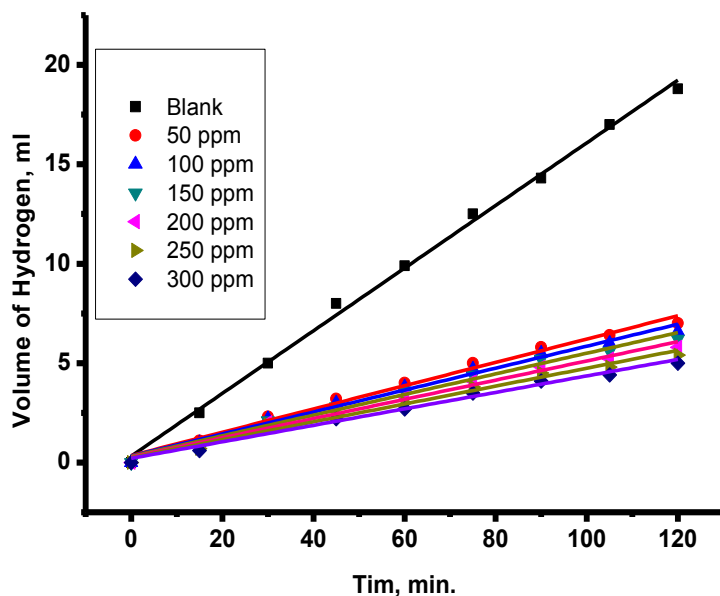


Figure 6. Hydrogen volume produced versus time curves with various doses of drug at 25°C

Slika 6. Zapremina vodonika proizvedena u odnosu na vremenski raspored sa prepoznatljivom centralizacijom inhibitora na 25°C



### 3.3. Electrochemical Techniques

#### 3.3.1. Open circuit potential ( $E_{\text{OCP}}$ )

From the Fig. 7 and Table 7 are shown several interesting points:

1. The  $E_{\text{OCP}}$  in the blank solution started at -522.8 mV then shifted anodically and the steady state is occurred after 300 S. This indicates that the initial dissolution process (the attack on the surface of metal) and then the formed oxide film.

2. In the presence of Lidocaine, the  $E_{\text{OCP}}$  started at relatively positive potential compared with that in the absence of the drug and then shifted anodically that starting from 521.7, 517.4, 513.7, 512.7, 510.4 and 507.8 mV according to the increasing the doses 50, 100, 150, 200, 250 and 300 ppm respectively. The steady state is attained rapidly, compared with the blank. Increasing the dose of the Lidocaine, make shift in the open circuit potential that increases in the active direction, this means that the drug might acts mainly as mixed type inhibitor [53]. The classification of a compound as an anodic or cathodic type inhibitor, based on the  $E_{\text{OCP}}$  displacement; if the shift in  $E_{\text{OCP}}$  is at least

$\pm 85$  mV compared to the one measured in the blank solution it can be classified as an anodic or cathodic inhibitor. However, from Fig. 7, the shift in  $E_{\text{OCP}}$  on adding Lidocaine is about 15 mV revealing that the present drug acts mixed type inhibitor but, slightly more as anodically inhibitor.

Table 7.  $E_{\text{OCP}}$  of the MS in the nonexistence and in existence of Lidocaine drug at 25°C

Tabela 7.  $E_{\text{OCP}}$  MS u odsustvu i prisustvu leka Lidokain na 25°C

| Conc.(ppm) | - $E_{\text{Min}}$ (mV) | - $E_{\text{Max}}$ (mV) |
|------------|-------------------------|-------------------------|
| Blank      | 522.8                   | 503.7                   |
| 50         | 521.7                   | 498.2                   |
| 100        | 517.4                   | 500.4                   |
| 150        | 513.7                   | 500.4                   |
| 200        | 512.7                   | 498.5                   |
| 250        | 510.4                   | 500.0                   |
| 300        | 507.8                   | 496.8                   |

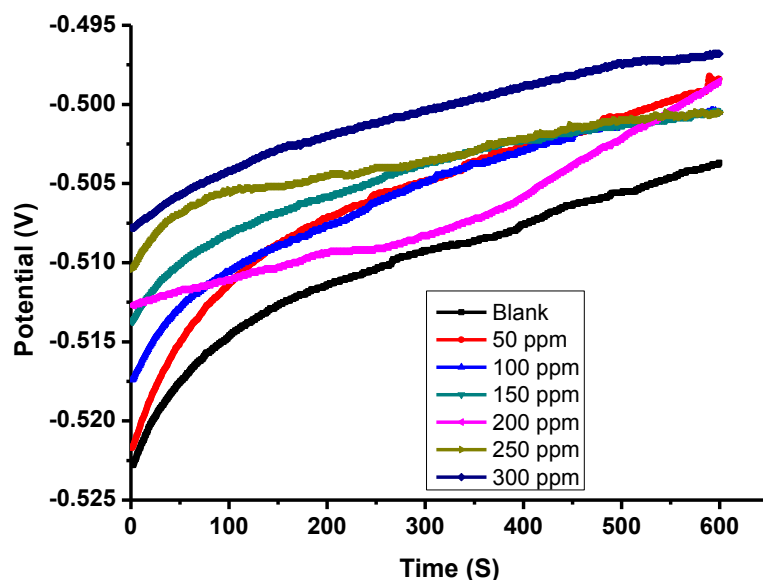


Figure 7. Open circuit potential,  $E_{\text{OCP}}$  vs. time curves for MS submerged in 1M HCl in the nonexistence and existence of Lidocaine drug at 25°C.

Slika 7. Potencijal otvorenog kruga,  $E_{\text{OCP}}$  u odnosu na vreme za MS potopljenu u 1M HCl u odsustvu i prisustvu leka Lidokain na 25°C.

### 3.3.2. Potentiodynamic polarization (PP)

The results are showing in nonexistence and with existence different doses of Lidocaine drug in Fig. 8. The obtained potentiodynamic polarization parameters are given in Table 8. These results indicating that the cathodic and anodic curves obtained according to Tafel-type behavior. The form of the curves is slightly similar either in the cathodic or in the anodic side, which indicates that

the mechanisms of MS dissolution and hydrogen reduction apparently remain in the presence of the inhibitor. Addition of Lidocaine decreased both the cathodic and anodic current densities and caused mainly parallel displacement to the more negative and positive values respectively, i.e. the presence of Lidocaine in solution inhibit both the hydrogen evolution and the anodic dissolution processes with overall shift of  $E_{\text{corr}}$  to slightly less negative values

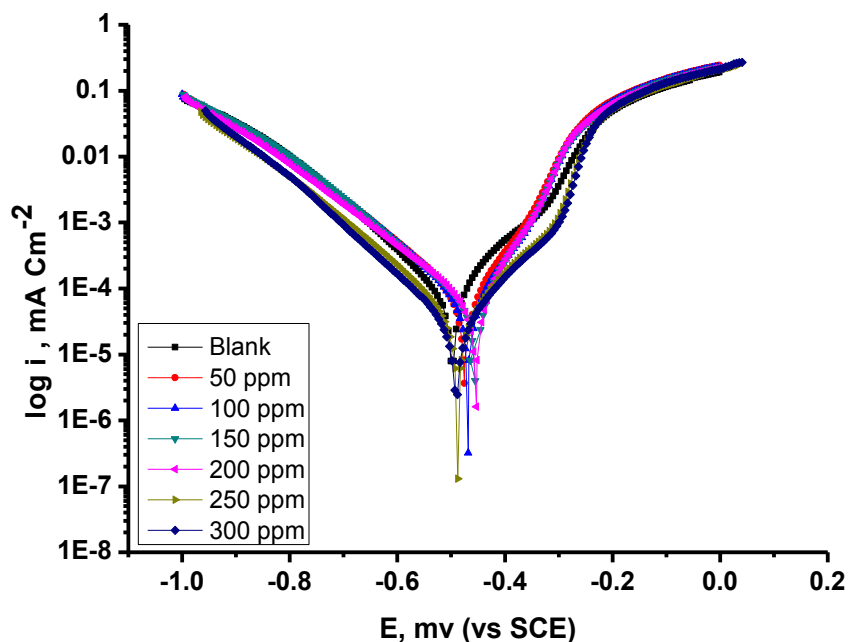


Figure 8. PP curves for the corrosion of MS in 1M HCl in the nonexistence and existence of various doses of Lidocaine at 25°C

Slika 8. PP krive za koroziju MS u 1M HCl u prisustvu i odsustvu različitih doza idokaina na 25°C

Table 8. PP parameters ( $E_{\text{corr}}$ ,  $i_{\text{corr}}$ ,  $\beta_a$  and  $\beta_c$ ),  $\theta$  and % IE in nonexistence and with existence various doses of Lidocaine in 1M HCl medium at 25°C

Tabela 8. PP parametri ( $E_{\text{corr}}$ ,  $i_{\text{corr}}$ ,  $\beta_a$  and  $\beta_c$ ),  $\theta$  i % IE u prisustvu i odsustvu različitih doza Lidokaina u 1M HCl medijumu na 25°C

| Conc. ppm | $i_{\text{corr}}$ mA/cm <sup>2</sup> | $-E_{\text{corr}}$ mV(SCE) | $\beta_a$ mV dec <sup>-1</sup> | $\beta_c$ mV dec <sup>-1</sup> | C. R. Mpy | $\theta$ | % IE |
|-----------|--------------------------------------|----------------------------|--------------------------------|--------------------------------|-----------|----------|------|
| 0.0       | 147.0                                | 498                        | 153                            | 344                            | 67.2      | ----     | ---- |
| 50        | 70.0                                 | 474                        | 99                             | 139                            | 31.99     | 0.524    | 52.4 |
| 100       | 69.2                                 | 468                        | 107                            | 159                            | 31.62     | 0.530    | 53.0 |
| 150       | 66.9                                 | 454                        | 70                             | 237                            | 30.59     | 0.545    | 54.5 |
| 200       | 65.2                                 | 454                        | 83                             | 180                            | 29.81     | 0.556    | 55.6 |
| 250       | 35.9                                 | 488                        | 131                            | 142                            | 16.84     | 0.749    | 74.9 |
| 300       | 34.4                                 | 491                        | 146                            | 159                            | 15.73     | 0.766    | 76.6 |

The graphical also show that the anodic and the cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) were slightly changed on increment of the doses of the Lidocaine. This means that the Lidocaine is mixed type inhibitor. It obvious that no change of the mechanism of inhibition in existence and nonexistence of Lidocaine drug, due to the cathodic and anodic Tafel lines are parallel. The values of Tafel slope is not higher refer to the diffusion process instead of the kinetic-controlled process [54]. The values of the cathodic slope that obtained from the electrochemical measurements confirm the hydrogen evolution reaction was activation or cathodic controlled [55].

The addition of the inhibitor did not modify the mechanism of this process but appears that the inhibition mode of the Lidocaine was used by simple adheres of the surface by adsorption process.

### 3.3.3. Electrochemical Impedance Spectroscopy (EIS)

The Nyquist and Bode impedance diagrams studies between 0.1 Hz and 100KHz frequencies rang abundance signal at  $E_{OCP}$  for MS in 1M HCl in the nonexistence and with existence of various doses of Lidocaine were obtained. The equivalent circuit that describe for metal and electrolyte are seen in Fig. 9, EIS variables and (% IE) were determination and recorded in Table 9.

Table 9. Electrochemical kinetic variables obtained by EIS technique for MS in 1M HCl without and with various doses of Lidocaine at 25°C

Tabela 9. Elektrohemijske kinetičke promenljive dobijene EIS tehnikom za MS u 1M HCl bez i sa različitim dozama Lidokaina na 25°C

| Conc. ppm | $R_p$<br>$\Omega \text{ cm}^2$ | $C_{dl}$<br>$\mu\text{F cm}^2$ | $\theta$ | % IE  |
|-----------|--------------------------------|--------------------------------|----------|-------|
| 0.0       | 80.5                           | 594.2                          | -----    | ----- |
| 50        | 162.6                          | 50.82                          | 0.505    | 50.5  |
| 100       | 168.7                          | 43.49                          | 0.523    | 52.3  |
| 150       | 172.0                          | 30.20                          | 0.532    | 53.2  |
| 200       | 182.5                          | 29.39                          | 0.559    | 55.9  |
| 250       | 239.0                          | 23.47                          | 0.663    | 66.3  |
| 300       | 294.8                          | 20.40                          | 0.727    | 72.7  |

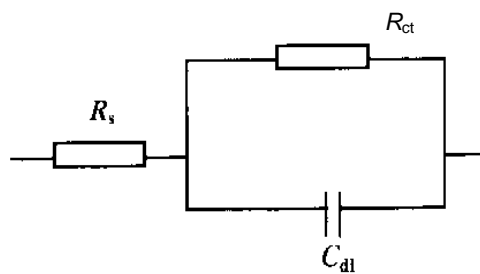
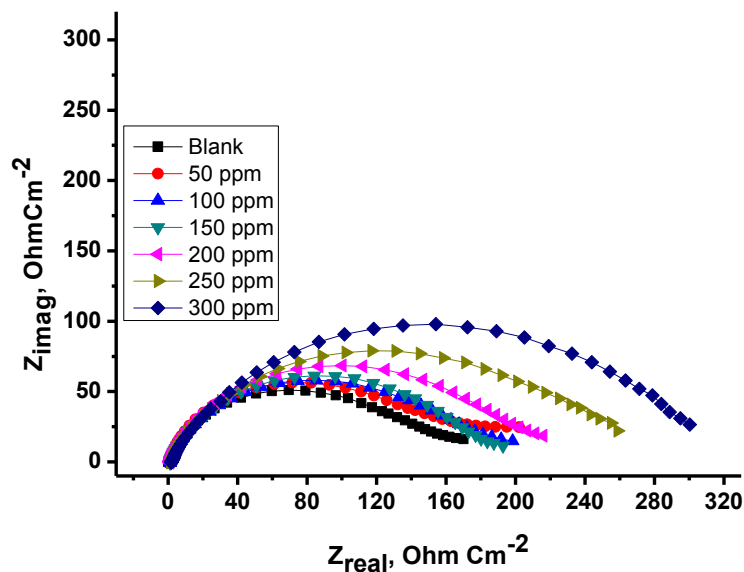


Figure 9. Electrical equivalent circuit model used to fit the experimental results,  $R_s$  is solution resistance and  $R_{ct}$  is charge transfer resistance

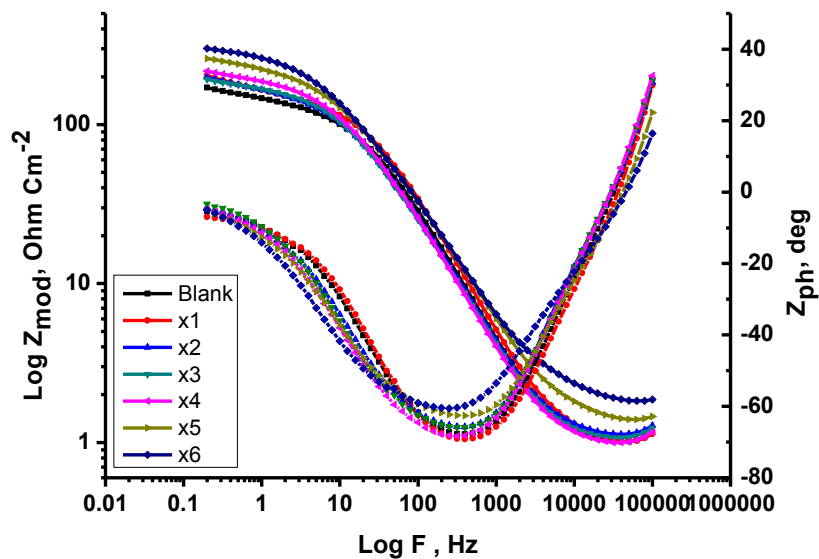
Slika 9. Model ekvivalentnog električnog kola koji se koristi za polaganje eksperimentalnih rezultata,  $R_s$  je otpor rastvora, a  $R_{ct}$  otpor prenosa naelektrisanja

The obtained Nyquist and Bode plotting for Lidocaine is shown in Fig. 10 a,b. Nyquist spectrum is characterized by a single full half-circle. This shows that the corrosion of mild steel is controlled by a charge transfer process [56]. The diameters of the capacitive loop obtained increase in the presence of Lidocaine. This indicated that the increasing in the inhibition efficiency of the corrosion process [57].

It was observed from the obtained EIS data that  $R_p$  increases and  $C_{dl}$  decreases with the increasing of inhibitor doses. The increase in  $R_p$  values gives increasing of the inhibition efficiency, due to the increase of the thickness of double layer and /or gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adherence film on the metal surface. This suggests that the coverage of the metal surface by the film decreases the double layer thickness. Also, this decreasing of  $C_{dl}$  with increasing the drug dose occurs as a result from a decrease in local dielectric constant and replacement water molecules by inhibitor molecules which, indicating that the inhibitor was adsorbed on the surface of both anodic and cathodic sites [58].



a) Nyquist



b) Bode

Figure 10. a, b The Nyquist (a) and Bode (b) plots for corrosion of MS in 1M HCl in the nonexistence and with existence of various doses of Lidocaine at 25°C

Slika 10. a,b. Nyquist (a) i Bode (b) krive za koroziju MS u 1M HCl u odsustvu i prisustvu različitih doza Lidokaina na 25°C

### 3.3.4. Electrochemical Frequency Modulation technique (EFM)

EFM is regarded a very good technique to determine the corrosion information directly and quickly because EFM is nondestructive technique to determine the corrosion [59]. The measurements data of EFM are became a valid data when the

practical causality factors (CF2 and CF3) are equals or near the hypothetical values (2 and 3) which determined from the frequency spectrum of the current reaction. Fig.11, illustrated the EFM inter-modulation spectrum of MS in 1 M HCl in nonexistence and existence of deferent doses of Lidocaine drug. It is clearly that, the treatment EFM

data utilizing two various models: (1) the activation model by solving three nonlinear equations and assuming no change of the corrosion potential due to the polarization of the working electrode (2) cathodic reaction controlled by complete diffusion [60].

The corrosion current density ( $i_{\text{corr}}$ ), the ( $\beta_a$  and  $\beta_c$ ) and (CF2 and CF3) are calculated from the two large peaks of inter-modulation spectrum, and are listed in Table 10. It is obviously, that the addition

of tested Lidocaine drug at given doses to the corrosive medium reducing the ( $i_{\text{corr}}$ ), indicating that, the Lidocaine drug inhibits the corrosion of MS by the adsorption process. The (CF2 and CF3) are equal or near the hypothetical values (2 and 3) indicative of that, the estimation information data are valid and with good values [61]. The % IE<sub>EFM</sub> values are increments by expanding the doses of Lidocaine drug, which determination and recorded in Table 10.

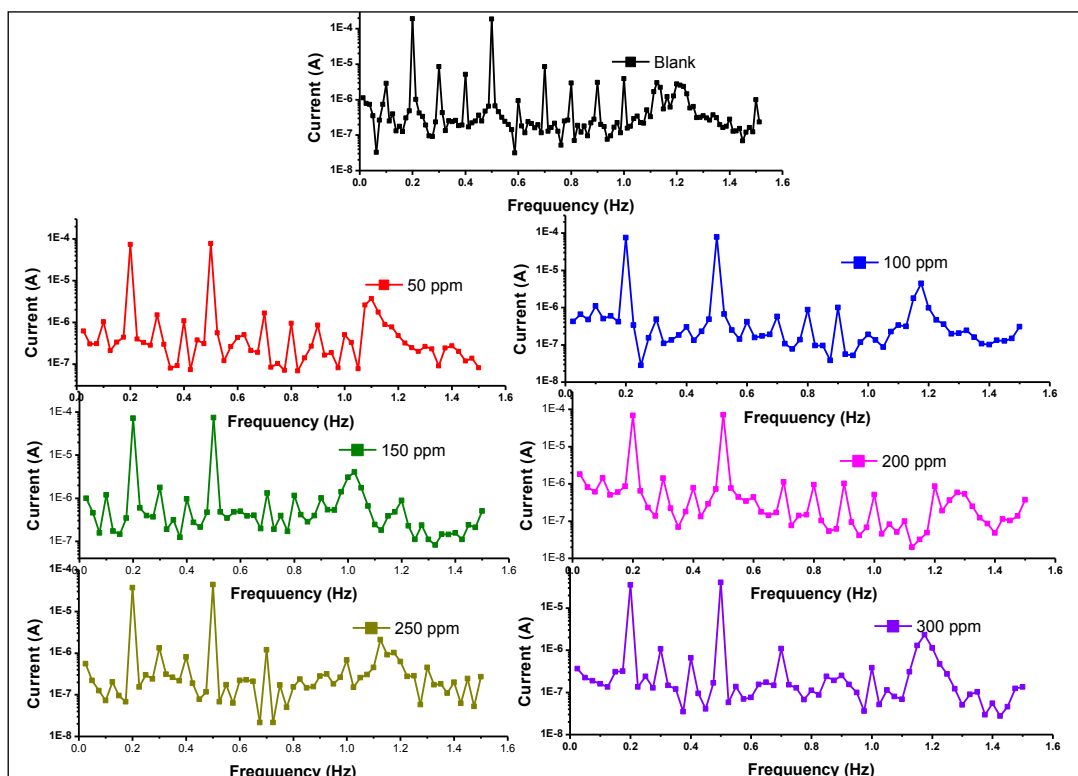


Figure 11. EFM for MS in 1M HCl unlucky deficiency and vicinity of distinctive convergences of Lidocaine

Slika 11. EFM za MS u 1M HCl nedostatku i blizini prepoznatljivih konvergencija Lidokaina

Table 10. Electrochemical kinetic parameters obtained by EFM technique for MS in 1M HCl without and with various doses of Lidocaine at 25°C

Tabela 10. Elektrohemijski kinetički parametri dobijeni EFM tehnikom za MS u 1M HCl bez i sa različitim dozama Lidokaina na 25°C

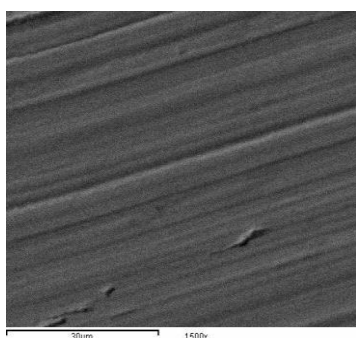
| Comp.     | Conc. ppm | $i_{\text{corr.}}$ $\mu\text{A cm}^{-2}$ | $\beta_a$ $\text{mV dec}^{-1}$ | $\beta_c$ $\text{mV dec}^{-1}$ | CF (2) | CF (3) | CR mpy | $\Theta$ | % IE |
|-----------|-----------|--|--------------------------------|--------------------------------|--------|--------|--------|----------|------|
| Blank     | 0.0       | 278.4                                    | 84.3                           | 110                            | 1.9    | 3.0    | 127.2  | ----     | ---- |
| Lidocaine | 50        | 128.7                                    | 103                            | 119                            | 2.0    | 3.3    | 58.9   | 0.537    | 53.7 |
|           | 100       | 121.3                                    | 100                            | 104                            | 2.2    | 2.7    | 55.4   | 0.565    | 56.5 |
|           | 150       | 108.9                                    | 91                             | 103                            | 2.9    | 2.1    | 49.8   | 0.608    | 60.8 |
|           | 200       | 100.6                                    | 89                             | 99                             | 1.9    | 2.6    | 45.9   | 0.639    | 63.9 |
|           | 250       | 88.95                                    | 125                            | 164                            | 1.7    | 1.2    | 40.6   | 0.681    | 68.1 |
|           | 300       | 65.95                                    | 102                            | 124                            | 2.1    | 3.9    | 30.1   | 0.763    | 76.3 |

### 3.4. Surface Examination

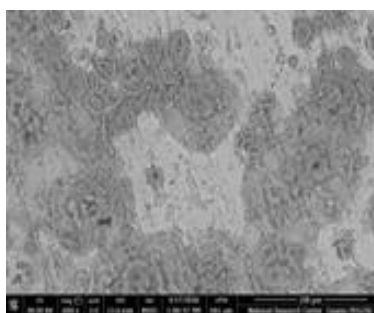
#### 3.4.1. Scanning Electron Microscopy (SEM) test

The micrographs that obtained for MS specimens in nonexistence and in existence of 300 ppm of Lidocaine drug after exposure for immersion one day in corrosive medium. It is clear that MS is suitable surfaces for corrosion attack in the blank sample or in corrosive medium only Fig. 12 a,b,c,. When the Lidocaine is existence in the corrosive medium, the morphology of MS surfaces is quite different from the previous one, and the specimen surface was smoother. It is clear that the

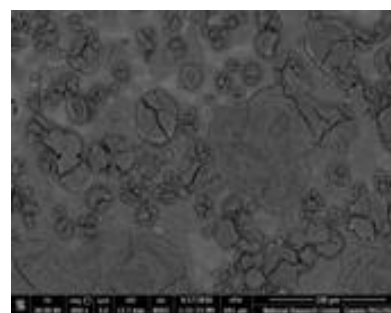
formation of a thin layer film adsorbed on the metal surface, which distributed in order way on the whole surface of the MS. This may be due to the adsorption of the Lidocaine on the MS surface and made up the passive film in order to block the active site present on the MS surface. The Lidocaine molecule interaction with active sites of MS surface, resulting in a decrease in the contact between MS and the corrosive medium and sequentially exhibited excellent inhibition effect [62].



(a) Free



(b) Blank in 1M HCl



(c) In 1M HCl with existence 300 ppm of Lidocaine

Figure 12 a,b,c. SEM micrographs for MS in the nonexistence and existence of 300 ppm of Lidocaine after submersion for 1 day

Slika 12 a,b,c. SEM mikrofografije za MS u odsustvu i prisustvu 300 ppm Lidokaina nakon potapanja tokom jednog dana

#### 3.4.2. Energy Dispersion Spectroscopy (EDX) [63]

To determine the elements and molecules that exist or adsorbed on the surface of MS after one day immersion in acid with optimum doses of Lidocaine by using the EDX spectra. Fig. 13, gives the EDX analysis of MS in 1 M HCl with in the presence of 300 ppm of Lidocaine. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of some Lidocaine). These data show that the carbon, nitrogen and oxygen atoms covered the specimen surface. The EDX analysis indicate that only nitrogen, carbon and oxygen are detect and show that the passivation film contained the chemical formula of Lidocaine drag adsorbed on the surface of MS. It is clear that, the percent mass of adsorbed elements N, C and O were present in the spectra and recorded in Table 11.

Table 11. Surface composition (% mass) of MS after one day of immersion in 1M HCl without and with the 300 ppm of Lidocaine

Tabela 11. Sastav površine (% mase) MS nakon jednog dana potapanja u 1M HCl bez i sa 300 ppm Lidokaina

| (Mass %)  | Fe    | C    | O   | N    | Cl   |
|-----------|-------|------|-----|------|------|
| Pure      | 98.28 | 0.78 | --  | --   | --   |
| Blank     | 72.1  | 9.23 | 17  | --   | 0.35 |
| Lidocaine | 55.23 | 16.5 | 7.1 | 22.5 | --   |



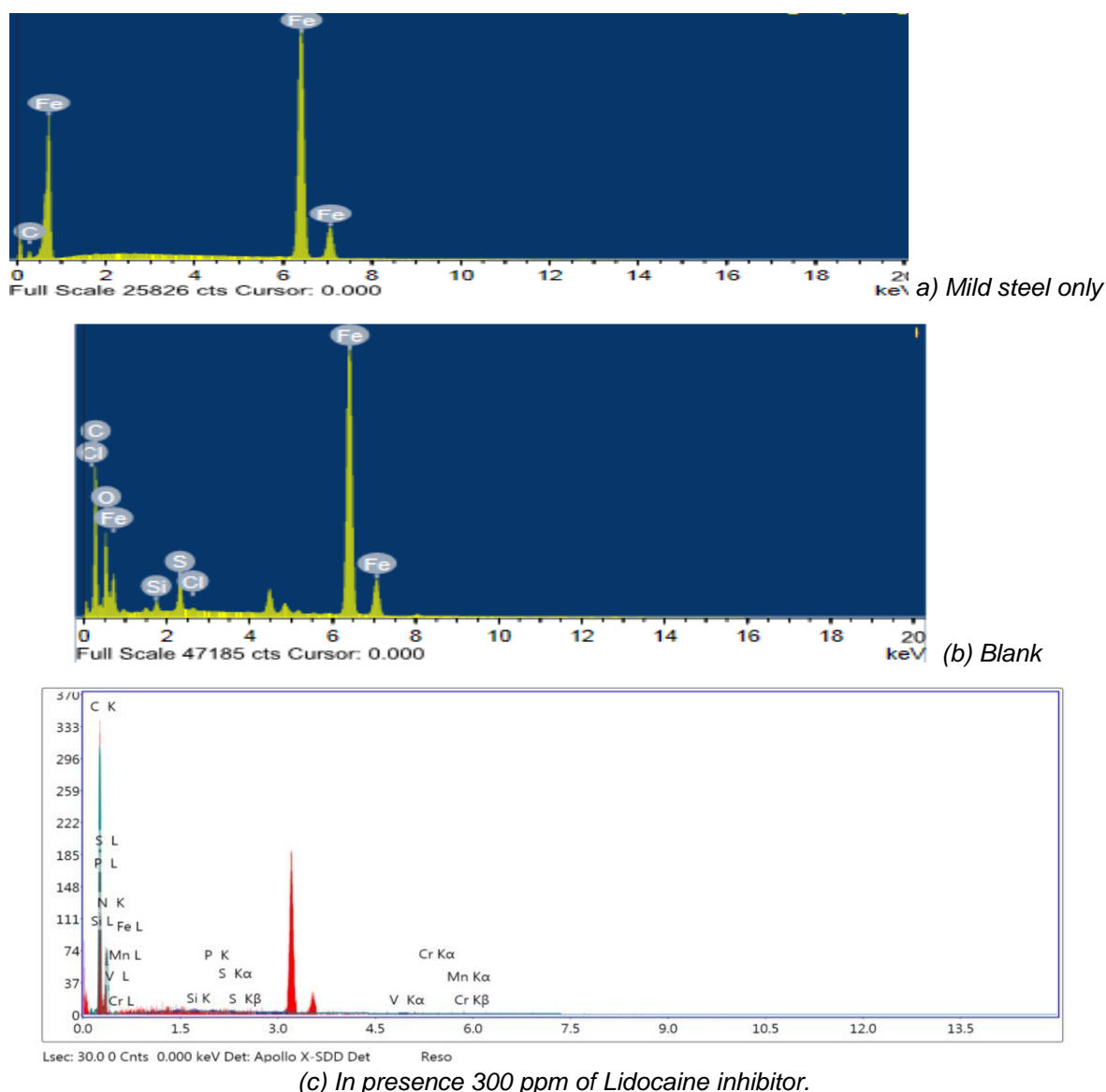


Figure 13 a,b,c. EDX analysis on MS in the presence and absence of Lidocaine for 1 day immersion

Slika 13 a,b,c EDX analiza na MS u prisustvu i odsustvu Lidokaina za 1 dan potapanj

### 3.4.3. Atomic Force Microscopy (AFM)

AFM is a powerful tool to investigate the surface morphology of various samples at nano-micro scale that is currently used to study the influence of corrosion inhibitors on metal solution interface. From the analysis, it can be gained regarding the roughness on the surface. The roughness profile values play an important role in identifying and report the efficiency of the inhibitor under study. Among the roughness, take a role in explanation about the nature of the adsorbed film on the surface [64-66]. Fig. 14a, shows the 3D images as well as elevation profiles of polished of MS in absence and present Lidocaine as an

inhibitor. It observed in Fig. 14b, that the surface of MS specimen (a) exposed to corroded solution affected vales structure with large and deep crack but the surface (b) revealed that the covering film is adsorbed on the metal surface. The conclusion, that the adsorption film can protect the surface of the metal from corrosion process. Analysis of the values indicated higher the values of roughness parameter reached. The mean roughness is found to be (2.60  $\mu\text{m}$ ) for the blank in acid solution which placed in 1M HCl one day and analyzed. The observation of the metal surface which immersed in 1M HCl in presence of 300 ppm of Lidocaine inhibitor possess roughness (259.14 nm) compared

to the blank solution. It can be noted that the value is lower than that of the blank value. The decrease in the roughness value reflected to the adsorption

of inhibitor molecule on metal surface thereby reducing the rate of corrosion.



Figure 14. a,b. The 3D of optical images of AFM in nonexistence and existence of Lidocaine drug

Slika 14. a,b. 3D optičke slike AFM u odsustvu i prisustvu leka Lidokain

#### 4.1. Mechanism of inhibition

To illustrate the mechanism of inhibition of corrosion on the MS surface in acid medium by using pharmaceutical drug compound as an inhibitor, it is must be know the nature of metal surface and the nature of the component of inhibitor structure. The MS is regarded the metal  $\alpha$ -phase [67], It is obvious that  $\alpha$ -phase state consists of grains and grain boundaries in the surface of the metal, Fig. 15. A cross-section of a piece or specimen of the metal that clarify both anodic and cathodic sites in the metal surface structure.

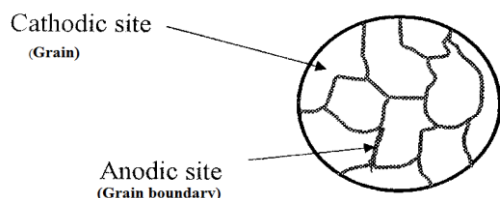


Figure 15. Schema models of metal  $\alpha$ -phase

Slika 15. Shematski modeli metalne  $\alpha$ -faze

The surface of MS is usually, coated with a thin film of iron oxide [68]. However, if this iron oxide film develops some cracks called anodic area are created on the surface, while other metal parts act as cathodes. It follows that the anodic areas are small surface, while nearly the rest of the surface of the metal large cathodes. Electrochemical corrosion involves flow of electric current between the anodic and cathodic areas like inter-granular corrosion Fig. 16. SEM image is shown the corrosion of MS in 1 M HCl after one day immersion that illustrated inter-granular corrosion.

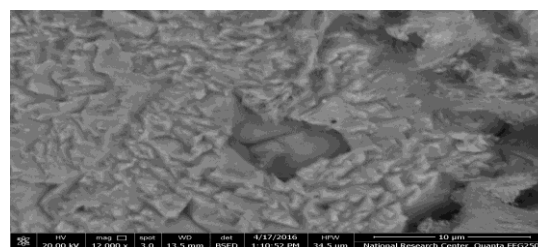


Figure 16. SEM image illustrated inter-granular corrosion after immersion the specimen in 1M HCl one day time.

Slika 16. SEM slika ilustruje međuzrnastu koroziju nakon potapanja uzorka u 1M HCl jednog dana.

All previous results prove that the Lidocaine drug under study was actually inhibits the corrosion of MS in HCl acid solution as a corrosive medium. The corrosion inhibition is due mixed type (physical and chemical) adsorption sue to the formation of a protected thin film that adsorbed on the MS surface.

The effect of Lidocaine drug under study as inhibitor may be corresponding to the accumulation of the inhibitor molecules on the metal surface, which prevent the direct contact of the metal surface with corrosive environment. The surface of the MS sample is positively charge in aqueous acid solution and possess vacant orbital [69,70]. The adsorbed  $\text{Cl}^-$  ions on MS surface turns it to negatively charged, then the protonated drug molecules get adsorbed on the negatively charged MS surface by electrostatic attraction (Physisorption) or donate the electron density to the vacant orbital of the metal surface in the form of neutral molecule, that involving displacement of water molecules from the metal surface and

sharing electrons between  $\pi$  bonding electron density, oxygen and nitrogen to the metal surface, the skeleton of inhibitor compound cover the cathodic sites and make thin layer to prevent

corrosion processes. The present of benzene ring, which has electrons density of  $\pi$ -bonding that enhancement the adsorption process and gives the very good inhibition efficiency [71] Fig. 17.

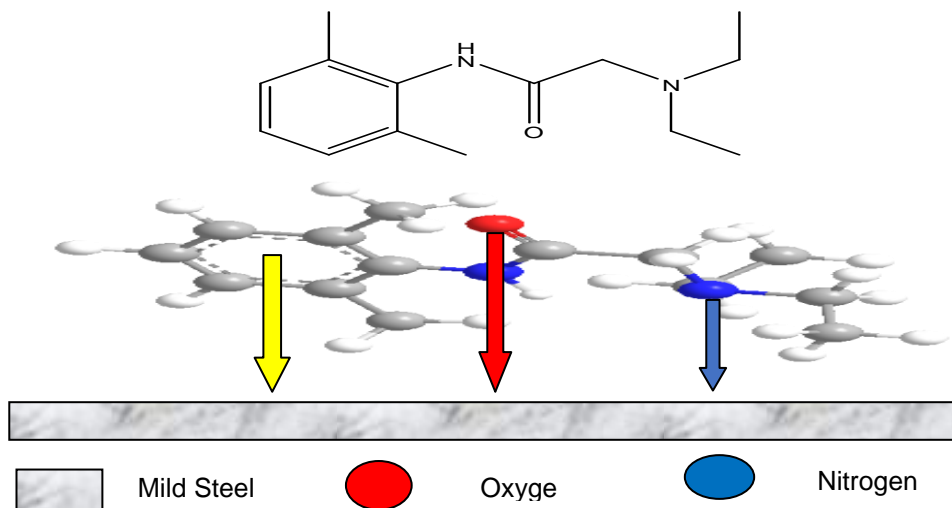


Figure 17. Schema model illustrate the mechanism of adsorption of Lidocaine drug on the surface of MS

Slika 17. Šema modela ilustruje mehanizam adsorpcije leka lidokain na površini MS

## 5. CONCLUSIONS

Inhibition of the corrosion of MS in 1M HCl solution by Lidocaine was determine by weight loss, hydrogen evaluation, potentiodynamic anodic polarization measurements, electrochemical impedance spectroscopy (EIS) and the electrochemical frequency modulation method (EFM). The surface of MS examination by Scanning Electron Microscopy (SEM), energy Dispersive X-ray (EDX) and atomic force microscopy (AFM). It was found that the inhibition efficiency depends on concentration, the mode of adsorption of the inhibitor and surface conditions. The observed corrosion data in presence of this inhibitor, namely:

1. The tested Lidocaine inhibitor established a very good inhibition for MS corrosion in 1M HCl solution,
2. Lidocaine inhibits the MS for the corrosion by adsorption on its surface and make thin film layer.
3. The inhibition efficiency of the tested compound increases with increasing the concentration.
4. Double layer capacitances decrease with increasing concentration of inhibitor. This fact may explained by adsorption of the inhibitor molecule on the MS surface.

5. The adsorption of Lidocaine drug on MS surface in HCl solution applied by Langmuir adsorption isotherm.

6. The values of inhibition efficiencies obtained from the different independent techniques used, showed the validity of the obtained results.

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## IZVOD

### ELEKTROHEMIJSKO PONAŠANJE PRI ZAŠTITI OD KOROZIJE MEKOG ČELIKA (MS) U 1M HCl KISELINI UPOTREBOM LEKA LIDOKAIN KAO INHIBITORA

*Lidokain, kao inhibitora korozije za zaštitu mekog čelik (MS) u 1M HCl, proučavan je ispitivanjem gubitka težine (VL), procene vodonika (HE), potencijala otvorenog kola (EOCP), potenciodinamičke polarizacije (PP), elektrohemijske impedansne spektroskopije (EIS) i elektrohemijske frekvencijske modulacije (EFM). Gubitak težine proučavan je na različitim temperaturama između (25 – 45°C) a procena vodonika i elektrohemijska ispitivanja na sobnoj temperaturi. Proučavan je uticaj temperature na inhibiciju korozije i izračunati termodinamički parametri aktivacije. Morfologija MS ispitivana je pomoću skenirajućeg elektronskog mikroskopa sa tehnologijom disperzivne rentgenske spektroskopije (SEM – EDKS) i atomskom mikroskopijom (AFM). Tehnika elektrohemijske impedance je pokazala da prisustvo leka lidokaina u rastvoru smanjuje dvoslojni kapacitet i povećava otpor prenosa naelektrisanja. Utvrđeno je da adsorpcija lidokaina na površini MS podleže izoterma Langmuir adsorpcije i razjašnjava mehanizam inhibicije korozije. Izračunati su parametri adsorpcije i utvrđeno je da lek lidokain deluje kao inhibitor mešovito tipa. Sva površinska ispitivanja i analize potvrđuju formiranje tankog filma koji je prekrio površinu metala i sprečava koroziju površine metala.*

**Ključne reči:** Adsorpcija; inhibicija; elektrohemijske tehnike; SEM; EDKS; AFM.

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