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Corrosion inhibition of carbon steel A 283 C using the acetylsalicylic acid

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Abstract: The corrosion inhibition characteristics of acetylsalicylic acid on carbon steel has been studied using electrochemical measurements. Results showed that: The inhibition efficiency values give maximum inhibition at the concentration of 300 ppm and decrease back. They decreased with increasing temperature. Polarization studies showed that this compound is an anodic inhibitor for carbon steel in decanted water from a tank bottom hydrocarbon storage (East Region Transport: Skikda Algeria). The inhibition occurs through adsorption of the inhibitor molecule on the metal surface. The adsorption of the inhibitor on the metal surface is found to obey Langmuir's adsorption isotherm. The values of thermodynamic parameters, such as K_{ads}, ΔG°_{ads}, ΔH°_{ads} and ΔS°_{ads} are calculated.

Keywords*:* Corrosion, Carbon Steel, Acetylsalicylic Acid, Inhibition, Decanted Water, Adsorption.

I. Introduction

Carbon steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining. These applications usually induce serious effect on equipments, tubes and pipelines [1-3]. The protections of these materials are generally secured by inhibitors used for their rapid action. Particularly organic compounds containing heteroatoms are usually employed. Generally, they act by adsorption on the metal surface which takes place through heteroatoms such as: nitrogen, oxygen, phosphorus, sulphur, triple bonds or aromatic rings…. The interactions between an organic inhibitor and a metal surface are principally physical adsorption and/or chemisorptions [4-14]. Recently, many studies are interested at the investigation of pharmaceutical compounds. In fact, these compounds offer interesting possibilities for corrosion inhibition and are of particular interest because of their safe use, high solubility in water and containing electronegative atoms in their molecules. These compounds should be good corrosion inhibitors [16-16].

Based on the foregoing points, the aim of this work is to study the inhibition efficiency of the acetylsalicylic acid **fig.1** in decanted water from a tank bottom hydrocarbon storage (East Region Transport: Skikda Algeria) using chemical (polarization and impedance) measurements. The mode of adsorption and the corrosion inhibition, mechanism are also discussed.

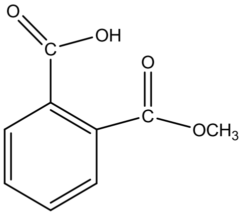

Fig .1: Scheme of acetylsalicylic acid

II. Experimental section

The electrochemical measurements are carried out with a three-electrode assembly: a platinum electrode against a reference electrode saturated calomel electrode and the working electrode of 1 cm^2 cross-section, made in the laboratory from steel pipes. The steel selected in this study is a carbon steel A283 grade C according to ASTM whose composition is as follows: C = 0.18%, S = 0.05%, P = 0.06%, Cu = 0.20% and Fe. Before the measurements, the electrode is polished successively with emery paper up to 1200 grade, then rinsed with distilled water, cleaned and degreased with acetone and dried in the open air.

The corrosive medium is decanted water in the bottom of storage tank of crude oil (Transport Region of Skikda Algeria). The physico-chemical characterization of the water is given in table 1. The electrochemical measurements were performed using a VoltaLab 40, with a PGZ301 potentiostat controlled by a computer and software VoltaMaster 4.

Table1: *The physico-chemical characterization of the decanted water*

Parameters	**Values**
pH	5.7
conductivity (mS/cm)	134.4
TDS (g/l)	67.1
Resistivity(Ω.cm)	7.44
SO_4^{2-} (mg/l)	300
S^{2-} (mg/l)	0.051
Cl^- (mg/l)	40750
O_2 dissolved	7.4
Bart test (bacterial corrosion)	Negative

III. Results and discussion

III.1. Polarization measurements

Fig. 2 represents potentiodynamic polarization curves for carbon steel in decanted water in the absence and presence of various concentration of acetylsalicylic acid. As can be seen the addition of the inhibitor molecules inhibit the metal dissolution.

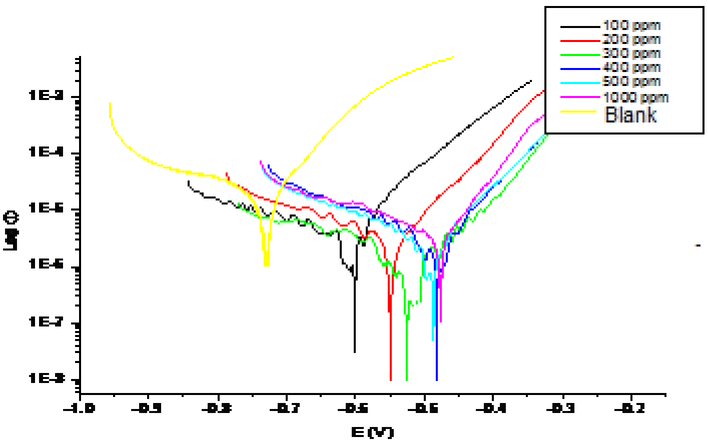

Fig 2: Polarization curves of carbon steel in decanted water in the absence and various concentrations of inhibitor

Table 2 shows the electrochemical corrosion parameters, such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), obtained by extrapolation of the tafel lines and the inhibition efficiency (IE%) which was evaluated from the relation:

$$IE\% = (I_0 - I_1/I_0)\,x100 \qquad (1)$$

Where I_0 and I_1 are uninhibited and inhibited current densities respectively. The obtained efficiencies given in table 2 indicate that the acetylsalicylic acid act as effective inhibitor. The addition of this compound induces a decrease in current and in the presence of this compound the corrosion potentials shifted to the positive direction compared to the uninhibited alloy. So, it could be concluded that the acetylsalicylic acid is an anodic inhibitor of carbon steel in decanted water. Furthermore, the corrosion inhibition efficiencies show a maximum efficiency (97%) at a concentration of 300 ppm, table 2.

***Table 2**: The electrochemical parameters of carbon steel in decanted water containing different concentrations of inhibitor at 25°C.*

Inhibitor concentration (ppm)	E_{corr}(mv)	I_{corr}(□A/cm^2)	Θ	%IE
0	-729.4	7.5371	-	-
100	-601.1	1.425	0.810	81.09
200	-549.3	0.914	0.878	87.87
300	-527	0.324	0.9705	97.05
400	-483.2	0.5025	0.933	93.33
500	-487.9	0.6584	0.912	91.26
1000	-476.7	2.335	0.690	69.01

III.2. Adsorption Isotherm

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor [17].

The dependence of the degree of surface coverage Θ on the molar concentration of the inhibitor was calculated using the following equation:

$$\Theta = I_o - I_i/I_o \qquad (2)$$

The values of (ϴ) have been inserted in the table 2. The degree of surface coverage was found to increase with increasing the concentration of additive compound. The data were tested graphically by fitting it to Langmuir isotherm which is given by equation 3 [18].

$$C/\Theta = C+1/K \quad (3)$$

Where C is the inhibitor concentration (ppm) K is the adsorption equilibrium constant and ϴ is the degree of coverage in the metal surface. When C_{inh}/Θ (ppm) were plotted against C_{inh} (ppm) a straight line was obtained which suggest that the adsorption of inhibitor obeys the Langmuir adsorption isotherm **Fig 3.** The value of the equilibrium constant K has been calculated, then the standard free energy can be deduced by using equation 4.

$$K=(1/55.55)\exp(-\Delta G^\circ_{ads}/RT) \quad (4)$$

The negative value of ΔG°_{ads} (-34.832 kJ mol-1) indicate that adsorption of the inhibitor on the metal surface is spontaneous.

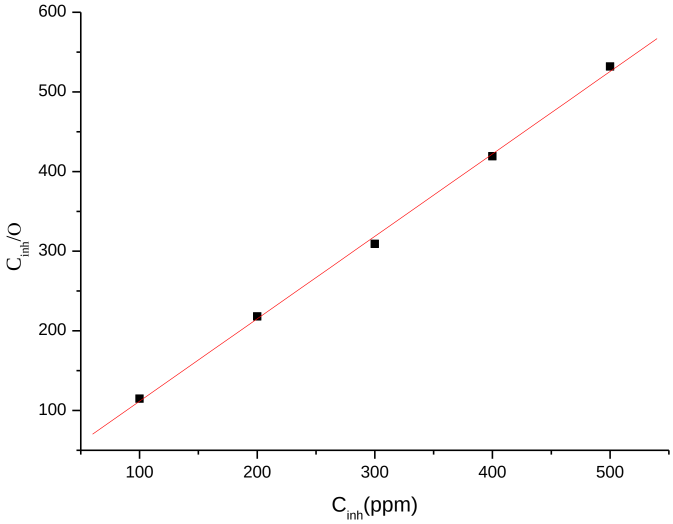

Fig.3. Plot of C_{inh}/Θ versus C_{inh} for carbon steel in decanted water solution in presence of different concentrations of inhibitor

Generally, values of ΔG°_{ads} around -20 kJ mol-1 or lower are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physisorption), those around -40 kJ mol-1 or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [19]. The value of ΔG_{ads} is less than 40 kJ mol-1 is commonly interpreted with the presence of physical adsorption by the formation of an adsorptive film with an electrostatic character [20-21]. However, some researchers have reported that adsorption of inhibitor molecules is obeying a comprehensive adsorption (physical and chemical adsorption) for the same values [22-23].

III.3. Effect of temperature

The effect of temperature on the various corrosion parameters E_{corr}, I_{corr}, k and IE was studied in decanted water at temperature range 25-40°C in the absence and presence of 300ppm of the inhibitor. The results were listed in table 3. An inspection of table 3 shown that as the temperature increases, the values of I_{corr} increases and IE decreases. This proves that the inhibition occurs through a physical adsorption on the metal surface.

Table 3: *The effect of temperature on the corrosion parameters of carbon steel in decanted water in absence and presence of 300ppm of inhibitor.*

Temperature °C	Concentration (ppm)	I_{corr}(mA.cm^{-2})	E_{corr}(mv)	k	%IE
25	0	7.5371	-729.4	85.92	-
	300	0.324	-527	2.532	97.05
30	0	39.242	-705.3	281.896	-
	300	5.1089	-403.4	36.7	80.95
35	0	55.905	-689.2	401.6	-
	300	14.913	-402.8	107.2	77.55
40	0	129.115	-663.5	927.5	-
	300	34.565	-400.7	248.3	73.22

The activation energy of the corrosion process was calculated using the following equation:

$$k=A\exp(-E_a^*/RT) \tag{5}$$

Where E^*_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant and k is the rate of metal dissolution reaction which is directly related to corrosion current density I_{corr} [24]. Plotting log(k) versus 1/T, the value E_a^* can be calculated from the slopes of straight lines obtained from fig 4. The values of E_a^* are listed in table 4.

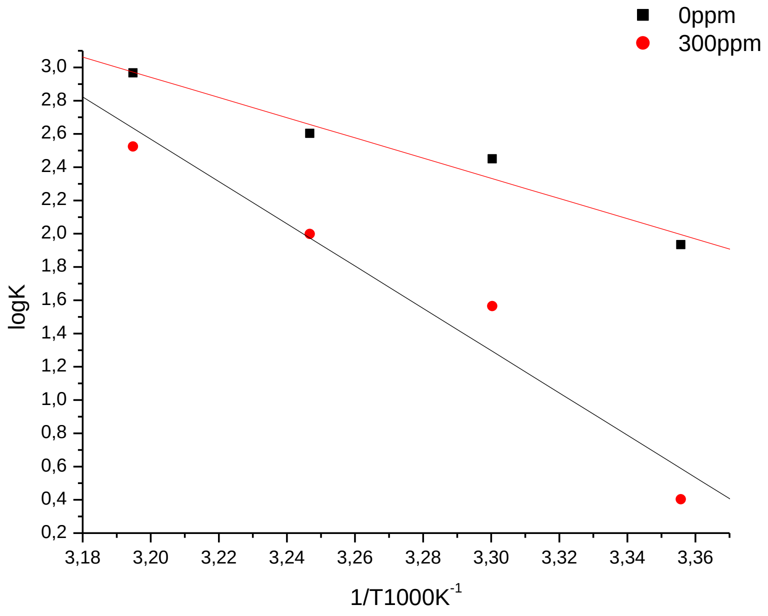

Fig.4. Plot of log (k) versus 1/Tx10^3, K^{-1} for carbon steel in decanted water Solution in absence and in presence of 300ppm of inhibitor.

The activation energy is higher in the presence of additives than in its absence. This observation further supports the proposed physisorption mechanism. Unchanged or lower values of E_a^* in inhibited systems compared to the blank have been reported to be indicative of chemisorptions mechanism, while higher values of E_a^* suggest a physical adsorption mechanism [25].This type of inhibitors retards the corrosion process at ordinary temperature whereas the inhibition is considerably decreased at elevated temperature [26, 27]. Plot of log (k/T) versus 1/T for carbon steel in decanted water in absence and presence of acetylsalicylic acid is shown in fig. 5.

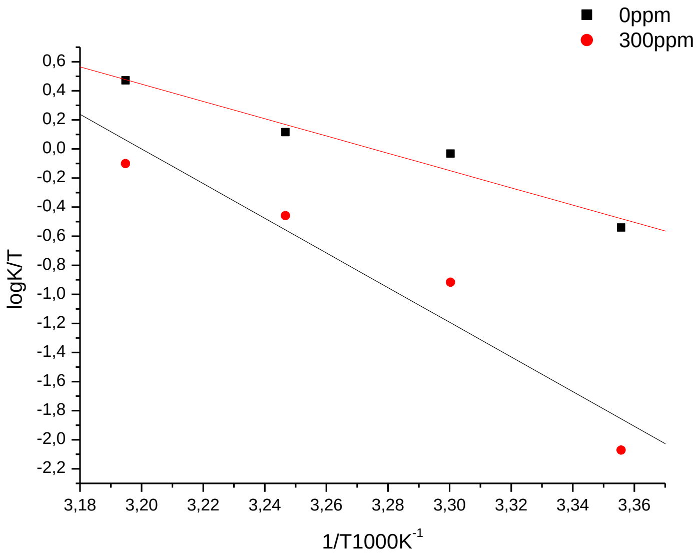

Fig.5. Plot of log (corrosion rate/T) versus 1/Tx10^3, K^{-1} for carbon steel in decanted water Solution in absence and in presence of 300 ppm of inhibitor.

As shown from this figure, straight line was obtained according to transition state equation (6):

$$\text{Rate}=RT/\text{Ɲ}h\ \exp(\Delta S^*/R)\ \exp(-\Delta H^*/RT) \qquad (6)$$

Where h is Plank's constant, Ɲ is Avogadro's number, ΔH^* is the activation enthalpy and ΔS^* is the activation entropy. The calculated values are given in table 4.

Table 4: Activation parameters of the corrosion of carbon steel 283 °K in decanted water in absence and presence of 300ppm of inhibitor.

Concentration (ppm)	Ea^*(J.mol^{-1})	ΔH^*(J mol^{-1})	ΔS^*(J.mol^{-1}K^{-1})
0	116.2679	113.7594	286.6372
300	230.735	228.9466	644.7087

These values indicate that the presence of the additive increases the activation enthalpy ΔH^* and the activation entropy ΔS^* for the corrosion process. The increase in the activation enthalpy (ΔH^*) in presence of the inhibitor implies that the addition of the inhibitor to the decanted water increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The entropy of activation (ΔS^*) in the blank and inhibited solution is large and positive. This increase in the entropy was caused by imperceptible replacement of water molecules due to the adsorption of inhibitor molecules on carbon steel, decreasing the extent of the dissolution reaction [28, 29].

III.4. UV-vis spectroscopic investigation

In order to confirm the possibility of the formation of inhibitor-Fe complex, UV-vis adsorption spectra obtained from the corrosive solution in the presence of different concentrations of acetylsalicylic acid after 3 h of the metal immersion are shown in fig 6. It is clearly seen that the charge transfer has been completely appeared and absorption maxima at 495nm indicating complex formation with Fe^{2+} ions which have a pink color. In Fig.7, we propose the *schematic representation of adsorption behavior of studied organic compound on carbon steel.*

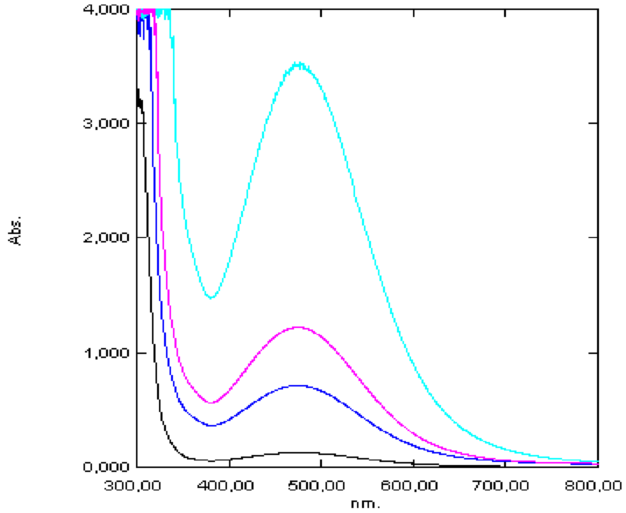

Fig.6. UV-spectra of the solutions containing different concentration of acetylsalicylic acid after 3h immersion of carbon steel.

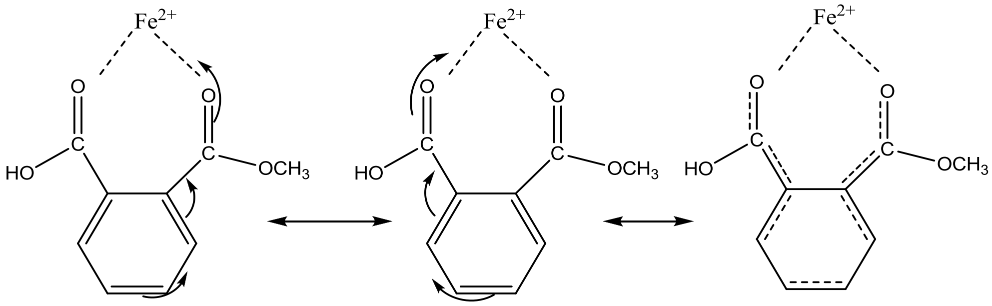

Fig. 7. Schematic representation of adsorption behavior of studied organic compound on carbon steel

III.5. Electrochemical impedance spectroscopy.

III.5.1. Effect of the inhibitor concentration.

In order to understand the inhibition behavior, electrochemical impedance spectroscopy was employed to investigate the influences of acetylsalicylic acid on the corrosion of carbon steel. Fig.8. presents Nyquist diagrams of the steel measured in absence and in presence of 300ppm of the inhibitor. The Nyquist plots consisted of two capacitive loops. The one at low frequency (in the right part of the figure) was related to change transfer resistance, which could correlate to resistance between the steel and outer helmoholtz plane [30-31]. Conversely the one at high frequency (in the left part of the figure) was attributed to the adsorbed film resistance due to adsorption of the inhibitor and all other accumulated products [32]. The EIS results were simulated using equivalent circuit shown in Fig.9. In this equivalent circuit, $R_s(R_1)$ is the solution resistance, R_p (R_p=R_f +R_{ct}) is the polarization resistance, Q_f and $R_f(R_2)$ are constant phase element and the resistance related to the surface film.

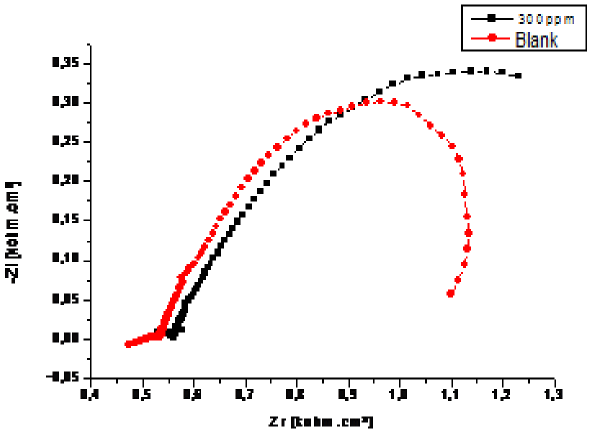

Fig.8. EIS of carbon steel in decanted water in absence and presence of 300ppm

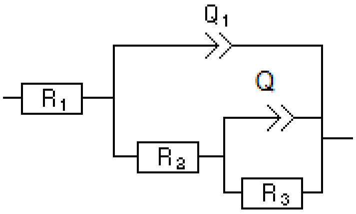

Fig.9. Equivalent circuit used to fit the EIS.

III.5.2. The effects of immersion time on the inhibitor performance.

To investigate the inhibitor adsorption kinetics and determine the time needed for the inhibitor to reach its maximum inhibition efficiency, EIS experiment were carried out in the presence of 300ppm of acetylsalicylic acid in decanted water at different immersion times at 25°C Fig 10.

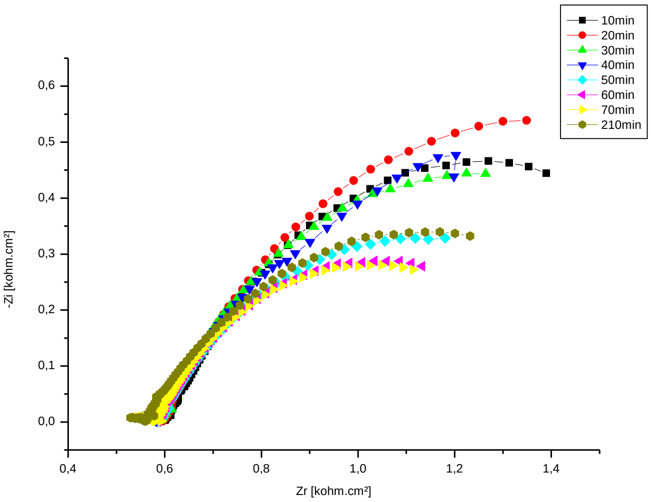

Fig.10. EISs of carbon steel in decanted water in presence of 300ppm of inhibitor at 25°C after different immersion times

A comparison of the results of R_f and R_p with 300ppm of inhibitor at different immersion times is presented in table 6.

Table.6. *EIS parameters obtained from the corrosion of carbon steel in decanted water containing 300 ppm of the inhibitor for different immersion times at 25°C*

Immersion time(min)	$Q_1(Fs^{-a)}$	a_1	R_f (Ohm)	Q (Fs^{-a})	a	R_p
0	0.427e-3	0,66	979	0.241e-6	0,794	785
10	0.356 e^{-3}	0.69	557	0.202 e^{-6}	0.63	1 360
20	50.19e-6	0.33	324	1.064e-3	0,71	1 707
30	4,415e-6	0.92	225	1.392e-3	0,672	2072
40	0.1341e-6	0,66	205	1.392e-3	0,67	1 690
50	0.1341e-6	0,67	223	1.114e-3	0.71	926
60	56.74e-6	0,66	285	1.136e-3	0.76	695
70	4,415e-3	0,42	354	1,188e-3	0,67	635
210	0.939 e-3	0,64	1118	7.697e-3	0.52	460

It can be seen that R_p increases in the first 30 minutes and then decreases. This is probably due to the formation of a corrosion product film on the metal surface in the initial stage of immersion. Extended immersion may lead to damage the film, probably because of the development of localized corrosion on the steel surface.

Q_f values are low and are consistent with the presence of a protective film on the metal surface formed by the inhibitor.

IV. Conclusion

1. The corrosion of carbon steel in decanted water can be inhibited using the acetylsalicylic acid.

2. The inhibition process follows Langmuir adsorption isotherm and corresponds to physisorption phenomenon.

3. The decrease in corrosion current density (I_{corr}) and the increase in inhibition efficiency (%IE) with increasing the additive concentration are proved that the tested compound act as inhibitor for carbon steel in decanted water.

4. Polarization studies showed that this compound is an anodic inhibitor for carbon steel in decanted water

5. The thermodynamic values obtained from this study E^*_a, ΔG°_{ads} indicate that the presence of the inhibitor increases the activation energy of corrosion and consequently decrease the rate of dissolution of carbon steel in decanted water. The negative value of ΔG°_{ads} indicates the spontaneous adsorption of the inhibition on the surface of carbon steel.

6. The UV-vis studies reveal the formation of the Fe-inhibitor complex which may be also responsible for the observed inhibition.

7. The equivalent circuit was selected based on properties of the EIS Nyquist diagrams

8. in the presence of the inhibitor, the double layer capacitance decreased which confirmed adsorption of the inhibitor molecules on the steel surface.

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