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# Effectiveness of Some Organic Compounds as Corrosion Inhibitors for Stainless Steel 201 in 1M HCl: Experimental and Theoretical Studies

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The corrosion inhibition of stainless steel 201 (SS 201) in 1M HCl in the existence of organic compounds (OC's) has been studied utilizing electrochemical tests (AC impedance (EIS), electrochemical frequency modulation (EFM), potentiodynamic polarization (PP)) and chemical tests (mass loss (ML)). The inhibition efficiency (IE) rises by increasing concentrations of testing compounds and lowered by raising the temperature. The obtained data exposed that this OC's adsorbed on the SS 201 surface following Langmuir isotherm. PP results showed that these organic compounds are mixed kind inhibitor. The surface analysis of the inhibited SS 201 was estimated by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The outcome data obtained from all tests are in best agreement.

Keywords: Corrosion inhibition, SS 201, HCl, PP, AFM, FTIR

# **1. INTRODUCTION**

Numerous metals and alloys, which utilized as a part of human activities, are powerless to various corrosion mechanisms because of their introduction in various corrosive media or condition to obtain stable compound [1-4]. Corrosion problem leads to economic damages in manufacturing [5]. Hydrochloric acid is widely useful in manufacturing in areas such as pickling of alloys including ferrous, industrial treating, petroleum refinery and oil well acidizing. SS201 is the significant engineering and creation material in the world due to its good mechanical manner. Hence, the utilize of SS 201 corrosion has requested the consideration of investigators to study ways to control the corrosion mainly in the solution including acid [6]. An OC's is outstanding for their productivities as

corrosion protection and those including "N" have frequently mentioned to in the literature [7-9], imines [10], dioxan-water mixtures [11], quaternary ammonium, salts based on 2-acetylallylchloride [12], 2-mercapto benzimidazole [13], Ethoxylated fatty alcohols[14], Schiff base compounds [15], pyrrole and its derivatives [16], Pyrazolocarbothioamide[17], 1,3-Thiazolidin-5-one [18], Pyrazolone [19], Distyryl [20]. The choices of these OC's have constructed on: a) are extremely soluble in the test solution, and b) enclose functional polar groups and wide conjugation in the form of aromatic ring amongst which they can adsorb on the SS201surface.

The aim of this paper is to study the protective action of some organic compounds (OC) towards the corrosion of SS 201 in 1M HCl using electrochemical and non-electrochemical tests. Also, the surface examination of the SS 201 has been studied.

#### 2. MATERIALS AND METHODS

# 2.1. Materials and solutions

The composition of SS201 in mass % is

Element	С	Mn	S	Р	Si	Cr	Ni	Ν	Fe
Type 201	0.15	5.5 - 7.5	0.03	0.060	1.0	16 - 18	3.5 - 5.5	0.25	rest

#### 2.2. Inhibitors

The inhibitors were prepared in the research laboratory agreeing to an earlier designated investigation method, categorized and purified by NML, IR spectra and elemental analysis have previously used. The structural formula of the studied inhibitors is recorded in Table 1.

Table 1. Chemical constructions, names, molecular weights and formula of the studied OC.

Inhibitor	Structures, Names	Mol. Formulas, Mol. Weights
A	OH $HO$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> 270.33



#### 2.3. Chemicals and solutions

The SS 201 coins utilized as working anode for electrochemical tests. The corrosive solution used is of analytical reagent HCl 37% with distilled water and its concentration has checked by standard solution of Na<sub>2</sub>CO<sub>3</sub>. Stock solutions ( $10^{-3}$  M) of each OC have achieved by dissolving of a specific measured amount material in fitting volume with DMF, then complete with absolute ethanol to the point of concentrations required ( $1 \times 10^{-6} - 21 \times 10^{-6}$ M). The OC inhibitors that used as a part of this research have listed in Table1.

#### 2.4. Tests used for corrosion estimations

#### 2.4.1. Mass loss (ML) tests

The used square coins of SS 201 with size  $2 \times 2 \times 0.2$  cm for ML test. The sample was first scratching to a mirror by use (200, 600 and 1200) coarseness emery paper, submerged in (CH<sub>3</sub>) <sub>2</sub>CO lastly washed with bi-distilled water and dried before being massed and soaked in the test solution. The mass reduction test has finalized in a 100 ml capability glass beaker set in water thermostat that contained 100 ml of 1M HCl existence and nonexistence of appending of unlike concentrations of examining OC. The entire corrosive medium was air openings. Following three clocks soaked the sample were obtained, splashed, dried, and massed exactly. The normal ML of the SS 201 sheets could be gotten. The  $\theta$  and IE% and the of OC for the corrosion of SS 201 were measured as in Eq. (1)

% IE =  $100 \ge \theta = 100 \times [(W^{\circ} - W)/W^{\circ}]$ 

Where W<sup>o</sup> and W are the data of the average ML without and with the OC, correspondingly.

(1)

#### 2.4.2. Potentiodynamic polarization tests

PP tests had completed in a traditional three-electrode cell with Pt as the auxiliary electrode  $(1.0 \text{ cm}^2)$  and SCE joined to a fine Luggin tube as a reference electrode. The working electrode was a specimen from SS 201 sheet of equivalent piece implanted in epoxy resin that the level surface area was  $(1.0 \text{ cm}^2)$ . The working electrode was pretreated as in ML tests before use.

#### 2.4.3. Electrochemical impedance spectroscopy (EIS) tests

EIS test was achieved by employing AC signals of 5 mV signal to signal amplitude at the OCP in the frequency series of 100 kHz to 0.1 Hz. All EIS information fitted with proper, proportional circuit utilizing the Gamry Echem Analyst programmer.

The (% IE) and ( $\theta$ ) of the investigated compounds got from the EIS tests can be computed from eq. (2) [21]:

% IE = 100 x  $\theta$  = 100 x [1 – (R°<sub>ct</sub> / R<sub>ct</sub>)]

Where  $R_{ct}^{\circ}$  and  $R_{ct}$  are the resistances nonexistence and existence inhibitor, consistently

# 2.4.4-Electrochemical frequency modulation (EFM) tests

EFM tests had achieved by the decision for the frequencies of range 2 and 5Hz [22]. The greater signal has utilized to obtain parameters (icorr), ( $\beta_c$  and  $\beta_o$ ) and CF-2 and CF-3 [23]. Every test has done by using Gamry apparatus PCI300/4 Galvanostat/Potentiostat/Zra analyzer. The software Analyst Echem 5.5 for fitting and computing data was used.

#### 2.4.5. Surface study

Surface investigation of SS 201 samples is soaked in numerous test solutions for a full day, after scratching mechanically employed by altering emery papers up to 1500 sizes. Then, after this time, the sample was cleaned, lightly with bidistilled water, dried and kept for analysis by utilizing FTIR and AFM. AFM is turning into a known test for roughness examination [24].

#### **3. RESULTS AND DISCUSSION**

# 3.1. Potentiodynamic polarization estimations

Figure 1 shows PP plots ( $E_{corr}$  versus log  $i_{corr}$ ) for SS 201 corrosion in test medium without and with various concentrations of compound (A). Similar curves were received for other compounds (not displayed). The corrosion parameters ( $i_{corr}$ ,  $E_{corr}$ ,  $\beta_a$  and  $\beta_c$ ) measured by PP method are recorded in Table 2. The corrosion parameters ( $i_{corr}$ ,  $E_{corr}$ ,  $\beta_a$  and  $\beta_c$ ) calculated from PP tests are listed in Table 2. The % IE obtained from pp method was calculated using the relation as follows:

(2)

% IE = 100 x  $\theta$  = 100 x [( $i_{corr} - i_{corr(inh)}$ ) /  $i_{corr}$ ] (3)

Where  $i_{corr}$  and  $i_{corr(inh)}$  are current densities obtained from uninhibited and inhibited solution, consistently.

As shown from Figure 1, the cathodic and anodic reactions of SS 201 were affected after addition of OC to test the solution. So, the addition of OC lowered the corrosion of SS 201 and delay the hydrogen evolution reaction. From Table 1, the values of  $i_{corr}$  were reduced with a rise in inhibitor concentration, and hence, % IE values improve. It is found that, there is a slight shift in corrosion potential, with no definite trend in the shift of  $E_{corr}$  values with improve in inhibitor concentration compared to that of blank solution, i.e. OC act as a mixed-type inhibitors [25]. The cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ) changed when the inhibitor added to the test solution. This points out that the anodic and cathodic reaction sites are delayed by a change in their mechanisms. The order of OC according to % IE is being: A > B > C.



**Figure 1.** PP Curves for the SS 201 corrosion in 1M HCl with and without of various concentrations of compound (A) at 25°C

**Table 2.** Results obtained from the PP of SS 201 in 1M HCl include various concentrations of studied OC at 25°C

Comp	Conc.,	i <sub>corr,</sub>	- E <sub>corr,</sub>	β <sub>a</sub>	β <sub>c</sub>	C.R		% IE
	$x10^{6} M$	$\mu A \text{ cm}^{-2}$	mV vs SCE	mV dec <sup>-1</sup>	mV dec <sup>-1</sup>	mpy	θ	
Blank	0.0	5310	448.0	120.3	152	25.4		
	1	594	498.0	110	135	7.7	0.888	88.8
	5	525	494.0	115	149	3.1	0.901	90.1
А	9	461	501.0	101	132	2.5	0.913	91.3
	13	398	466.0	100	148	2.3	0.925	92.5
	17	366	470.0	112	136	1.8	0.931	93.9

	21	307	477.0	114	131	0.8	0.942	94.2
	1	982	472	111	142	9.9	0.815	81.5
	5	876	476	127	149	8.5	0.835	83.5
D	9	812	481	120	132	3.6	0.847	84.7
D	13	738	486	95	131	2.9	0.861	86.1
	17	509	489	90	129	2.4	0.904	90.4
	21	419	493	98	128	1.8	0.921	92.1
	1	1226	448	115	141	11.6	0.769	76.9
	5	1003	473	125	140	9.3	0.811	81.1
~	9	939	466	116	141	5.1	0.823	82.3
С	13	876	471	115	135	4.3	0.835	83.5
	17	764	466	125	133	3.8	0.856	85.6
	21	594	470	121	131	2.5	0.888	88.8

3.2. Impedance (EIS) measurements



**Figure 2.** EIS Bode and Nyquist plans for SS 201 in 1M HCl before and after addition of various concentrations of compound (A) 25°C



Figure 3. Equivalent circuit consumed to the EIS value in 1M HCl.

Comp	Conc., x 10 <sup>6</sup> M	$R_{ct}, \Omega$	$C_{dl},\ \mu Fcm^{-2}$	θ	%IE
Blank	0	23	393		
	1	251	142	0.908	90.8
	5	268	92	0.914	91.4
•	9	309	82	0.926	92.6
A	13	316	80	0.927	92.7
	17	365	78	0.937	93.7
	21	480	68	0.952	95.2
	1	131	145	0.824	82.4
	5	152	110	0.859	84.9
D	9	159	102	0.855	85.5
D	13	183	95	0.874	87.4
	17	260	83	0.932	91.2
	21	345	77	0.933	93.3
	1	101	154	0.772	77.2
	5	124	117	0.815	81.5
C	9	137	112	0.832	83.2
C	13	146	100	0.842	84.2
	17	170	94	0.865	86.5
	21	220	84	0.895	89.5

**Table 3.** Data are obtained from EIS tests for SS 201 in 1.0M HCl before and after addition of various concentrations of studied compounds (A-C) at 25°C

Figure 2 shows the Nyquist and Bode diagrams obtained from the SS 201 at corresponding corrosion potentials after half hours dissolved in 1M HCl after and before addition of concentrations of compound (A). The same compound curves were acquired for other OC (not displayed). As the concentration of inhibitor rises the diameter of the semi-circle rises. EIS data of the OC were tested applying the equivalent circuit, Figure 3 [26, 27]. The C<sub>dl</sub>, for a circuit containing a CPE data ( $Y^0$  and n) were measured from eq. (4) [28]:

$$C_{dl} = Y^0 \omega^{n-1} / \sin[n(\pi/2)]$$

(4)

Where  $\omega = 2\pi f_{max}$ ,  $f_{max}$  is the maximum frequency. The semi-circle diameter measures the charge transfer resistance,  $R_{ct}$ . Improve in  $R_{ct}$  refers to increase in the width of the double layer that adsorbed by inhibitor [29]. The value of the ( $C_{dl}$ ) decreases by including inhibitor into aggressive solution. Also,  $C_{dl}$  can be measured by the next eqn.:

$$C_{dl} = \varepsilon \varepsilon_o \left( A / \delta \right) \tag{5}$$

Where  $\varepsilon$  is the double-layer dielectric constant and  $\varepsilon_0$  the vacuum electrical permittivity [30]. The outcome data obtained from EIS were listed in Table 3. The order of IE% obeys: A> B > C.

# 3.3. Electrochemical frequency modulation (EFM) tests

EFM intermodulation spectra of SS 201 dissolution in the test solution existence and nonexistence of diverse concentrations of compound (A) at 298 K are displayed in Figure 4. The

%% IE<sub>EFM</sub> obtained from EFM technique was calculated. The corrosion parameters gotten from EFM method are shown in Table 4. It is found that,  $i_{corr}$  decreases with increasing organic compound concentrations, and therefore, %IE<sub>EFM</sub> values increase. The causality factors (CF-2 and CF-3) are found close to the standard values (2.0 and 3.0), and therefore, the values obtained from this technique are valid [31]. The %IE<sub>EFM</sub> obtained from EFM technique is the same sequence of ML, EIS and PP methods, whereas: A > B > C



**Figure 4.** EFM data for SS 201 in 1M HCl in the with and without of various concentrations of compound (A) at 25°C

Table	4.	Parameters	obtained	from	EFM	tests	for	SS	201	before	and	after	adding	various
	cor	ncentrations of	of compou	nds (A	-C) in	1M H	Cl							

Comp	Conc., $x$ $10^6 M$	$i_{corr,}$ $\mu A \ cm^{-2}$	$egin{array}{c} eta_{a,} \ mVdec^{-1} \end{array}$	$egin{array}{c} eta_{c}, \ mVdec^{-1} \end{array}$	C.R , mpy	CF- 2	CF-3	θ	%IE
Blank	0.0	3788	103.2	116.0	173	2.1	3.1		
	1	359	89.1	100.3	61.5	2.7	3.3	0.905	90.5
	5	295	97.9	109.8	52.1	1.90	2.8	0.919	91.9
	9	280	89.0	99.54	49.1	2.31	2.8	0.928	92.8
A	13	276	75.3	96.23	45.7	1.8	2.9	0.937	93.7
	17	238	91.6	101.9	24.6	1.70	2.8	0.943	94.3
	21	181	98.3	117.2	20.0	2.1	3.1	0.958	95.8
	1	640	99.2	125.9	77.7	1.9	2.8	0.831	83.1
	5	549	84.8	116.5	62.1	1.8	3.4	0.855	85.5
В	9	515	81.3	111.1	54.2	2.0	2.8	0.864	86.4
	13	443	79.2	115.7	50.8	1.9	3.4	0.883	88.3
	17	299	81.9	117.9	30.1	1.8	3.1	0.921	92.1

	21	219	97.5	115.0	28.8	1.9	3.1	0.942	94.2
С	1	810	95.6	105.6	120.4	1.9	3.2	0.786	78.6
	5	640	89.0	110.4	100.2	1.9	3.4	0.831	83.1
	9	587	93.0	107.1	105.2	2.1	3.1	0.845	84.5
	13	526	90.1	100.8	87.1	2.1	3.1	0.861	86.1
	17	443	92.8	109.7	84.5	2.1	3.1	0.883	88.3
	21	375	94.1	110.9	58.5	1.9	3.2	0.901	90.1

# 3.4. ML measurements

The ML of SS 201 coins in 1.0M HCl solution after and before additive of various concentrations from the calculated OC, was calculated after 180 min of inundation at 25 ±1°C. Figure 5 signifies this for compound (A). The same curves were obtained from other compounds (not existing). The outcome values of %IE are gotten in Table 5 at various concentrations from the OC at 25°C. The data exhibited that the presence of OC lowers the ML and the CR. The (%IE) and then  $\theta$ , of the calculated compounds for the corrosion of SS 201 were calculated from eq. (1) [32]. IE%, followed by these OC, have lower in the order: A > B > C.



**Figure 5.** Plot (Time –ML) for the dissolution of SS 201 with and without various concentrations of compound (A) at 25°C

**Table 5.** % IE for all OC at 120 min immersion for SS 201 in 1M HCl solution after and beforeaddition of various concentrations of studied compounds as measured from ML tests

Comp	ŀ	A	В		С		
Conc., x $10^6 M$	θ	% IE	θ	% IE	θ	% IE	
1	0.803	80.3	0.781	78.1	0.762	76.2	

5	0.864	86.4	0.822	82.2	0.801	80.1
9	0.871	87.1	0.843	84.3	0.812	81.2
13	0.886	88.6	0.865	86.5	0.835	83.5
17	0.893	89.3	0.893	89.3	0.858	85.8
21	0.903	90.3	0.899	89.9	0.876	87.6

# 3.5. Temperature effect

It was established that the IE reduced with improved temperature, as shown in Table 6, also the data from (Table 6) for compound (A) elucidates the adsorption lower with improving the temperature and CR, The same tables were achieved for other OC (not presented).

Figure 6 shows difference of IE of inhibitor (A) with various temperatures for SS 201 corrosion in 1M HCl, (alike curves were obtain, not displayed). The lowering of % IE with increasing the temperature was indicative for physical adsorption (physisorption).



**Figure 6.** Temperature influence on % IE at various concentrations of compound (A) for SS 201 corrosion in 1M HCl with different temperatures

**Table 6**. Data of % IE, ( $\theta$ ) and ( $k_{corr}$ ) for SS 201 corrosion after 120 min immersion in 1M HCl before and after addition of various concentrations of compound (A) at various temperatures

Temp.	Conc. [x10 <sup>6</sup> M]	Weight loss mg cm <sup>-2</sup>	$k_{corr}$ $mg \ cm^{-2} \ min^{-1}$	%IE
	Blank	5.99	4.99	
25	1	1.18	0.98	80.3
23	5	0.81	0.68	86.5
	9	0.77	0.64	87.2

	13	0.68	0.57	88.7
	17	0.64	0.53	89.3
	21	0.58	0.48	90.3
	Blank	7.50	6.25	
	1	1.86	1.55	75.2
	5	1.66	1.38	77.9
30	9	1.56	1.30	79.2
	13	1.47	1.23	80.4
	17	1.43	1.19	80.9
	21	1.30	1.08	82.7
	Blank	8.91	7.43	
	1	2.75	2.29	69.1
	5	2.69	2.24	69.8
35	9	2.52	2.10	71.7
	13	2.39	1.99	73.2
	17	2.28	1.90	74.4
	21	2.16	1.80	75.8
	Blank	11.91	9.93	
	1	5.51	4.59	53.7
40	5	5.11	4.26	57.1
40	9	4.97	4.14	58.3
	13	4.11	3.43	65.5
	17	4.39	3.66	63.1
	21	4.16	3.47	65.1
	Blank	13.74	11.45	
	1	6.18	5.15	55.0
	5	5.44	4.53	60.4
45	9	5.33	4.44	61.2
	13	5.12	4.27	62.7
	17	5.07	4.23	63.1
	21	4.96	4.13	63.9

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The energy of activation  $(E_{a}^{*})$  was obtained by Arrhenius eq. (6) [33]:

 $k_{corr} = A \exp(-E_a^* / RT)$ 

(6)

(7)

Where A = Arrhenius constant. The data of  $E_a^*$  can be gotten from the slope of the lines straight of relation 1/T vs log k<sub>corr</sub> (Figure 7) in the existence and nonexistence of OC at various temperatures is listed in Table 7. The effective  $E_a^*$  indicated greater data within the sight of these compounds than without them. Along these lines, retards the corrosion process at lesser temperatures, but this protective activity decreases in greater temperature. The measure effective  $E_a^*$  established that the studies compounds hindrance the corrosion more efficiently at higher concentrations. Likewise, rise in  $E_a^*$  with the appending of unlike concentrations of OC showing, increase the energy barrier for the corrosion reaction [34-35]. ( $\Delta S^*$ ,  $\Delta H^*$ ) are obtained from transition state eq. (7) [36]:

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

Figure 8 displays a plot of (1/T) vs. log ( $k_{corr}$  /T). Straight lines are reached to measure the data of  $\Delta H^*$  and  $\Delta S^*$  and listed in Table 7.

Usually, the  $\Delta H^*$  of a chemisorption process arrived (100 kJ mol<sup>-1</sup>) [37-38]. The –ve sign of  $\Delta S^*$  are showed that the activated complex in the rate-determining step prefers an association rather than dissociation [39].



Figure 7. Arrhenius designs of variation of log  $k_{corr}$  vs 1/T for the dissolution of SS 201 in 1M HCl without and with of various concentrations of compound (A)



Figure 8. Plots of (log  $k_{corr}$  / T) vs. 1/ T for the dissolution of SS 201 in 1M HCl before and after addition of various concentrations of compound (A)

 Table 7. Parameters for SS 201 dissolution in 1M HCl before and after addition of various concentrations of different OC

Comp	Conc., x 10 <sup>6</sup> M	E <sub>a</sub> *, kJ mol <sup>-1</sup>	$\Delta H^*$ , kJ mol <sup>-1</sup>	$-\Delta S^*$ , J mol <sup>-1</sup> K <sup>-1</sup>	
Blank	0.0	33.4	13.4	166.1	
	1	73.7	30.9	43.4	
	5	77.8	32.7	31.3	

А	9	80.5	33.8	23.6
	13	85.0	35.8	9.8
	17	90.4	38.1	4.1
	21	91.1	38.4	2.2
	1	72.8	29.2	44.2
	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	32.3		
В		24.2		
	13	84.2	33.0	14.8
	17	88.1	36.4	11.5
	21	89.8	37.7	3.4
	1	71.3	28.8	50.6
	5	75.0	30.4	39.6
С	9	76.3	30.3	36.1
	13	78.8	32.1	28.6
	17	83.2	35.2	15.2
	21	86.7	36.3	4.6

#### 3.7. Adsorption isotherms

The essential data on the interaction among the inhibitor and the SS 201 surface have obtained by the adsorption isotherm [40-41].

There are many isotherms, the best-fit Langmuir isotherm. Langmuir is obtained as follows [42].

$$C/\Theta = 1/K_{ads} + C$$
(8)

Where,  $K_{ads}$  is the adsorption constant equilibrium. Scheming (C) vs. (C/ $\Theta$ ) of OC at various temperatures is displayed in Figure. 9, alike curves were acquired for other compounds (not displayed). Table 8 shows the effect of temperature on adsorption for OC, the values of  $K_{ads}$  and  $\Delta G^o{}_{ads}$  are measured. The difference of the ( $K_{ads}$ ) of the inhibitors with their molar concentrations was measured conferring to Eq (8). The data gotten of  $K_{ads}$  and  $\Delta G^o{}_{ads}$  have obtained in Table 8. The equilibrium constant ( $K_{ads}$ ) of adsorption process determined using Eq. (9) Utilized to determine ( $\Delta G^o{}_{ads}$ ) as follows:

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

(9)

Where 55.5 is the molar water concentration in mol L<sup>-1</sup>. The  $\theta$  is straight forwardly identified with the execution of adsorption layer, which is an indirect function of the molecular organization. The  $\Delta G^{\circ}_{ads}$  and K<sub>ads</sub> data for OC computed and record in Table 8. The more negative  $\Delta G^{\circ}_{ads}$  data so that from the organized estimations of  $\Delta G^{\circ}_{ads}$  the request of IE is as per the following: A > B > C. The parameters gotten from adsorption procedure were given from these Figures are shown in Table 8. The data of  $\Delta G^{\circ}_{ads}$  are negative and improve as the % *IE* improved which led to that these examined compounds are powerfully adsorbed on the SS 201 surface and demonstration the spontaneity of the adsorption procedure. Usually, data of  $\Delta G^{\circ}_{ads}$  up to  $\Delta G^{\circ}_{ads}$  20 kJ mol<sup>-1</sup> are physical adsorption while those more negative than  $\Delta G^{\circ}_{ads}$  40 kJ mol<sup>-1</sup> are chemisorptions [43].

$$\Delta H^{\circ}_{ads}$$
 and  $\Delta S^{\circ}_{ads}$  can be measure from the next equation [44, 45] expressed by:  
 $Ln K_{ads} = \frac{-\Delta H^{\circ}_{ads}}{RT} + const$ 
(10)

Figure 10 demonstrations the plot of log K<sub>ads</sub> vs 1/T which obtain straight lines slope ( $-\Delta H^{\circ}_{ads}/2.303R$ ). Calculated data of  $\Delta H^{\circ}_{ads}$  and  $\Delta S^{\circ}_{ads}$  utilized eqn. (10, 11) were acquired.

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T \Delta S^{o}_{ads}$$
(11)

The data obtained from the adsorption of inhibitors were computed at temperature (30-  $55^{\circ}$ C) and are recorded in Table 8, which can explain the mechanism of corrosion inhibition [46], Negative data  $\Delta S^{\circ}_{ads}$  show that, there is a lower in the disorder of corrosion process on SS 201 surface in 1M HCl utilizing OC as corrosion inhibitors (Table 8) [48-49].







**Figure 10.** Variation of Log  $K_{ads}$  vs 1/T from Langmuir for the adsorption of inhibitor (A) in 1M HCl

Table 8. Adsorption thermodynamic parameters for OC at different	nt temperatures
------------------------------------------------------------------	-----------------

Comp	Temp., K	$-\Delta G^{\circ}_{ads}$ kJ mol <sup>-1</sup>	$-\Delta H^{\circ}_{ads}$ kJ mol <sup>-1</sup>	$-\Delta S^{\circ}_{ads}$ J mol <sup>-</sup> K <sup>1</sup>
	298	25.2		120
	303	23.4	56	109
Α	308	23.1		108

	313	22.5		106
	318	21.9		104
	298	24.3		107
	303	22.4		105
	308	22.1	54	104
В	313	21.4		103
	318	21.1		100
	298	22.8		106
	303	22.2		103
С	308	21.1	51	100
	313	20.9		98
	318	20.5		93

# 3.8. Atomic force microscopy (AFM) study

AFM technique is proceeded to investigate the surface morphology of SS 201 in the test solution without and with OC, and its important test for examining the surface roughness (Sa) of a sample [50]. Figure 11 shows AFM images (3D) for the blank and inhibited specimen of SS 201, correspondingly.

**Table 9.** The outcome data obtain from AFM roughness (Sa) of OC (A-C) at  $21 \times 10^{-6}$ M for 1 day at  $25^{\circ}$ C

Specimen	( <b>Sa</b> ) nm
Blank	512
(A)	147
(B)	172
(C)	183





**Figure 11.** AFM images (3D) of SS 201 immersed in 1M HCl only (blank) and SS 201 immersed in 1M HCl at  $21x10^{-6}$  M of OC (A-C) for 1 day at  $25^{\circ}$ C

The average roughness (Sa) can calculated from images of AFM. Table 9 gives the corresponding (Sa) value. A relative view of the above (Sa) table 9 obviously creates that the surface of the SS 201 is smoothened due to the formation of coating film [51].

3.9 FTIR analysis



Figure 12 FTIR spectra of inhibitor (A) stock solution (black line) and a layer of inhibitor (A) adsorbed on SS 201 surface (red)

Functional groups and characterizing covalent bonding knowledge had been identified by FT-IR which is an influential analytical device [52]. The finger print spectra of the OC (A) and the SS 201

surface after inundation in 1.0 M HCl +  $21 \times 10^{-6}$  to (A) for 180 min has achieved and compared to each other. It was obviously clear that similar fingerprint of OC (A) with the exception of the absence of any functional group and it suggested being due to reaction with acidic medium. (The same diagrams have achieved in the presence of the other OC, (not shown). From Figure 12 there are small moves in the peaks of the SS surface from the original peak of the stock OC solution, these moves indicate that there is an interaction among SS 201 and some of the OC molecules.

#### 3.10. Theoretical studies of inhibitors

The inhibition behavior of the investigated OC for SS 201 corrosion in acidic solution could be discussed by quantum chemical studies. The optimized geometry, frontier molecular orbital of HOMO, LUMO and the distribution of Mulliken charge of OC are diagrammed in Figure 13, respectively. It is seen that, the distributions of electron density were localized on HOMO and LUMO of inhibitors confirms the electron donating and accepting centers are possible in (OC) molecules. The detailed data of quantum chemical parameters for (OC) are calculated and listed in Table 10. The inhibition efficiency of investigating inhibitors for CS corrosion in acidic solution is related to the energy of lowest unoccupied molecular orbital (E<sub>LUMO</sub>), the energy of highest occupied molecular orbital (E<sub>HOMO</sub>) and the energy gap  $\Delta E$  ( $\Delta E = E_{LUMO} - E_{HOMO}$ ) [53]. From the Table 9, it can be noted that, the higher E<sub>HOMO</sub> values indicate that OC molecules can easily give electrons to the empty dorbital of iron. But, the lower E<sub>LUMO</sub> values show a higher electron accepting ability of the SS 201 metal. The smaller values of  $\Delta E$  show the stability of forming complex on the SS 201 surface [54]. Therefore, the reactivity order of OC for corrosion protection of CS according to  $\Delta E$  is A >B > C. Table 9 displays inhibitor (A) has the smallest  $\Delta E$  paralleled with the other OC molecules. Consequently, it could be expectable that compound (A) molecule has more disposition to adsorb on the SS 201 than the other OC. It was significant that the attendance of an electron donating such as -CH<sub>3</sub>, are more favored than absence of -CH<sub>3</sub> which raise the hindrance efficiency of the inhibitor. The HOMO and LUMO electronic density distributions of these molecules have planned in Figure 13 for the HOMO of the studied compounds that the benzene ring, N and O have a great electron density. The existing data in Table 9 display that the measured dipole moment lower from (A > B > C). From the quantum chemical analysis, it is found that, an agreement with the previously mentioned experimental data gotten by ML, EIS, PP, EFM measurements.

Inhibitor s	НОМО	LUMO	Mulliken Charges
A			



Figure 13. The frontier molecular orbital examined inhibitors (HOMO and LUMO).

Table 3. I arameter gotten nom quantum for examined compounds	Table 9.	Parameter	gotten	from	quantum	for	examined	compounds
---------------------------------------------------------------	----------	-----------	--------	------	---------	-----	----------	-----------

Inhibitor	Е <sub>номо</sub> (ev)	E <sub>LUMO</sub> (ev)	$\Delta E,$ $(ev)$ $(E_L-E_H)$	μ (Debye)
А	9.14	0.78	8.360	2.09
В	9.12	0.73	8.390	1.72
С	9.1	0.68	8.420	1.67

3.11. Comparison between inhibition efficiency results from the measurement technique used



**Figure 14.** Comparison of prevention efficiencies (verified using all tests at 25°C) obtained for corrosion of SS 201 in 1.0M HCl solutions including  $21 \times 10^{-6}$  of the studied inhibitors

The agreement between the results gotten from ML, PP, EIS and EFM studies confirmed that by increasing OC concentrations the inhibition efficiency increased. The obtained values of % inhibition efficiency of different experimental methods are shown in Figure 14. This diagram show the comparison of inhibition efficiency obtained for corrosion of SS 201 from different experimental methods.

#### 3.12 Corrosion hindrance mechanism

Four kinds of adsorption [55] may occur, including OC at the interface of SS 201– solution: 1) Electrostatic attraction among the charged molecules and metal; 2) Contact of unshared electron pairs in the OC with the SS 201; 3) The interaction of metal  $\pi$ -electrons; 4) Summation of all the above. From the outcome data obtained from the various tests, corrosion hindrance of SS 201 in 1M HCl solutions by the OC as designated from ML, PP and EIS tests were depended on the concentrations and the nature of the inhibitor. The sequence of IE is at: A > B > C. This order of the lowering in the IE of the tested compounds can be accounted for in terms of the polar effect [56]. A > B > C, this may be due to: the greater molecular size of (A) then (B) and (C), the existence of the number of  $-CH_3$  group in the molecules in addition to the these molecules may be protonated in the acid solutions and can be adsorbed on it changing its surface to be negatively charged one).

**Table 10.** Some organic compound as corrosion inhibitors by other authors for steel in HCl and in this study

Inhibitor	Structure	sample	IE%	References
1,4-Butanediamine	H <sub>2</sub> N NH <sub>2</sub>	Stainless steel 304	51	57
1,8-Octanediamine	$H_2NCH_2(CH_2)_6CH_2NH_2$	Stainless steel 304	58	57
Cetylpyridinium chloride	CI - N+ CH2(CH2)14CH3	Carbon steel	81	58
Cetylpyridinium bromide	N <sup>+</sup> Br <sup>−</sup> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub>	Carbon steel	87	58
4-Hydroxy coumarin	OH OH O	Mild steel	61	59
OC	present work	SS 201	95.8	This study

# 4. CONCLUSIONS

The tested OC (A-C) found a very good protection for SS 201 corrosion in acidic medium, where IE% improved by rising in a concentration of OC (A-C). The lessening in corrosion protection

with improving temperature led to desorption of the adsorbed inhibitor OC molecules takes place. OC hinders SS 201 corrosion by adsorption on its SS 201and obeys Langmuir isotherm. PP diagrams showed that organic compounds are mixed-kind inhibitor. Double layer capacitances ( $C_{dl}$ ) decreased with improving the inhibitor concentration added, while ( $R_{ct}$ ) rises. The outcome data of protection efficiencies obtained from the various tests utilized good agreement.

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