Corrosion Protection of C-Steel in Hydrochloric Acid Solutions Using Some Pharmaceutical Compounds

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ABSTRACT

The corrosion behavior of C-steel (CS) in 1M HCl and in the presence of pharmaceutical compounds, Pancuranium Bromide and Rocuronium Bromide, as Quaternary ammonium derivatives has been investigated using, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP), electrochemical frequency modulation (EFM) and weight loss (WL) techniques. Polarization curves show that, Pancuranium bromide and rocuronium bromide are mixed-type inhibitors. Results of EIS showed the increase in the charge transfer resistance and the decrease in the double layer capacitance.The adsorption isotherm of these compounds was found to be Temkin adsorption isotherm. Some thermodynamic parameters were computed and explained. It was found that the adsorption process increases, in the same direction as inhibition efficiency(%IE). The results indicated that the IE increases with increasing the concentration of inhibitors and decreases with increasing the temperature. Some quantum chemical parameters were calculated by the semi-empirical AM1 method to provide further vision into the mechanism of inhibition of the corrosion process. The results obtained from chemical and electrochemical techniques are in good agreement.

Keywords: C-steel (CS), EIS, SEM, Quaternary ammonium derivatives, Pancuranium Bromide, Rocuronium Bromide, HCl.

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INTRODUCTION

Corrosion of the CS is a major issue for many industries because of the chemical environment of the industrial processing. In many industries, acids such as hydrochloric, sulphuric or phosphoric are widely used for pickling, descaling, acid cleaning etc., The acids damage the materials under treatment. In this kind of situation, organic and inorganic inhibitors are used to reduce the corrosive property of acids [1-3]. A large number of organic compounds were studied as corrosion inhibitors, unfortunately most of the organic inhibitors used are very expensive and health hazards. Their toxic properties limit their field of application. Thus, it remains an important object to find cost-effective and non-hazardous inhibitors for the protection of metals against corrosion. The influences of nontoxic organic compounds on the corrosion of metals in acid media were investigated by several authors [4-12]. The use of drugs as corrosion inhibitors was investigated by several authors [13-20]
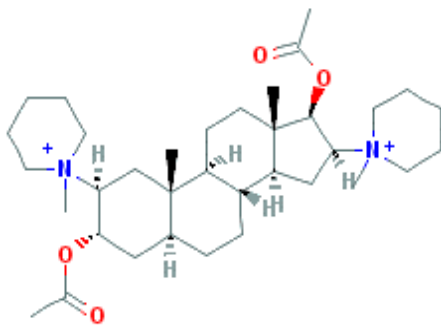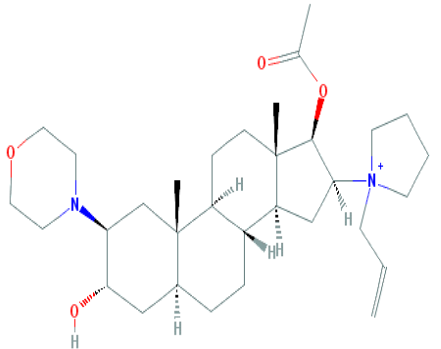
The significant of this paper is to develop new inhibitors for CS. For this purpose corrosion of CS has been investigated using various chemical and electrochemical techniques. The choice of these drugs as corrosion inhibitors are based on their natural origin as well as their non-toxic characteristics and negligible negative impacts on the aquatic environment.

MATERIALS AND METHODS

Materials: Tests were performed on CS specimens of the following composition in weight %: C 0.14, Cr 0.1, Ni 0.01, Si 0.024, Mn 0.5, P 0.05, S 0.05 and Fe rest.

Inhibitor: The pharmaceutical drugs, Pancuranium Bromide, (PAVULON), and Rocuronium Bromide, (ESMERON), have been investigated purchased from ORGANON pharmaceutical company

Table 1. The molecular structures, names, chemical formulas and molecular weights of the investigated drugs

Inhibitor	Structure	IUPAC Name	Molecular weight (g/mol)	Chemical formula
Pancuranium Bromide(PAVULON)		[(2S,3S,5S,8R,9S,10S,13S,14S,16S,17R)-17-acetyloxy-10,13-dimethyl-2,16-bis(1-methylpiperidin-1-ium-1-yl)-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl] acetate; dibromide	732.6699	$C_{35}H_{60}Br_2N_2O_4$
Rocuronium Bromide(ESMERON)		[(2S,3S,5S,8R,9S,10S,13S,14S,16S,17R)-3-hydroxy-10,13-dimethyl-2-morpholin-4-yl-16-(1-prop-2-enylpyrrolidin-1-ium-1-yl)-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl] acetate; bromide	609.6782	$C_{32}H_{53}BrN_2O_4$

Solutions: The aggressive solutions, 1M HCl were prepared by dilution of analytical grade (37 %) HCl with bi distilled water. The concentration ranges of the drugs used was 25-150 ppm.

Chemical Methods: Six parallel CS sheets of $2.0 \times 2.0 \times 2$ cm were abraded with various grade emery papers (200-320-500-800-1000) and then washed with bi distilled water and acetone. After accurate weighing, the specimens were immersed in a 250 mL beaker, which contains 150 mL of HCl with and without addition of different concentrations of investigated drugs, as inhibitors. Through period time 30

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min takeout coupons, washed, dried and re-weighted accurately through 3hr. at various temperatures from 298 to 328 K [21,22].The average weight loss of six parallel CS sheets could be obtained. The IE% and the degree of surface coverage, (θ) were calculated as follows by using equation (1) [23]:

$$IE\% = \theta \times 100 = [1-(W/W^{\circ})]\times100 \qquad (1)$$

Where, W° and W are the values of the average weight losses without and with addition of inhibitors; respectively. Corrosion rate was calculated using equation (2):

$$\text{Corrosion Rate } (k) = W/A \times T \qquad (2)$$

Where W is weight loss at certain time (t) in min. and (A) area in cm^2 [24]

Electrochemical Techniques: Electrochemical experiments were carried out using cell consists of three electrodes (a) Working electrode is $1cm^2$ CS welded with Cu-wire for electrical connection and mounted into glass tube of appropriate diameter and use epoxy resin to make the contact area of the electrode to be 1 cm^2. This electrode is abraded as before [25] (b) Reference electrode is saturated calomel electrode SCE. Used directly in contact with working solution, while all potential value was recorded Vs.SCE. Lugging-Haber capillary tube was also included in the design, Lugging capillary tip is made very close to the surface of the working electrode minimize IR drop [26] (c) Platinum foil ($1cm^2$) as auxiliary electrode. All electrochemical measurements were performed in solution 1M HCl in presence and absence various concentrations of Pancuranium Bromide, (PAVULON) and Rocuronium Bromide, (ESMERON) at 298K under un-stirred and aerated conditions. The measurements were performed using Gamry instrument Potentiostat / Galvanostat, ZRA(PCI4-G750), this include Gamry applications include DC105 software for DC corrosion, EIS300 software for electrochemical impedance spectroscopy, and EFM140 for electrochemical frequency modulation measurements along with computer for collecting data and analysis it by use Echem analyst V.6.03 used for plotting, graphing, and fitting the result data.

Non-destructive method: (a) EIS measurements were carried out in frequency range from 0.3 Hz to 100 kHz with amplitude of 5 mV peak to peak using Ac signals at open circle potential. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameter deduced from EIS analysis are R_{ct} charge transfer resistance, capacitance of double layer, C_{dl}. IE % and (θ) were defined by this equation (3):

$$IE \% = \theta \times 100 = [1-(R^{\circ}_{ct}/R_{ct})] \times 100 \qquad (3)$$

Where, R°_{ct}, R_{ct} are the charge transfer resistance in the absence and presence of inhibitors, Pancuranium Bromide, (PAVULON) and Rocuronium Bromide, (ESMERON) respectively [27].

(b) EFM measurements were carried out using two frequency 2 and 5 Hz. The base frequency was 0.1 Hz, so the wave form repeats after 1 sec. the higher frequency must me at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of double layer dose not contributes to the current response. Often 10 Hz reasonable limit. The inter modulation spectra contain current responses assigned for harmonically and inter modulation current peak. The large peaks were used to calculate the corrosion current density ($i_{corr.}$), the Tafel slopes (β_c and β_a) and the causality factors CF-2&CF-3 [28-29].

Destructive method: This method includes DC potentio dynamic polarization technique which was used to determine corrosion current density under steady state conditions by applying potential from -1500 to +500 mV to obtain Tafel polarization curve and the result current is plotted as logarithm scale vs potential related to SCE, extrapolating of two Tafel regions give ($i_{corr.}$) and ($E_{corr.}$) corrosion potential. By ($i_{corr.}$) we able to calculate rate of corrosion (R) = 0.13($i_{corr.}$) (Equivalent weight)/D. Where, D is density in g/cm^3 [30]. Equation (4) was used to determine IE% and (θ):

$$IE\% = \theta \times 100 = [1-(i_{corr}/i^{\circ}_{corr})] \times 100 \qquad (4)$$

where i_{corr} and $i^{\circ}_{corr.}$ are the corrosion current densities in the absence and presence of inhibitors, Pancuranium Bromide, (PAVULON), and Rocuronium Bromide, (ESMERON), respectively.

Surface analysis: Preparation of CS surface by keeping the coupons for 24 h. in 1M HCl in the presence and absence of inhibitors, Pancuranium Bromide, (PAVULON), and Rocuronium Bromide, (ESMERON),

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respectively, after abraded using different emery papers up to 2000 grade size then the coupons were washed gently with bi distilled water, carefully dried and mounted into desiccators without any further treatment. The corroded CS were examined using an X-ray diffractometer Philips (pw-1390) with Cu-tube (Cu Ka1, I = 1.5405 A°), scanning electron microscope (SEM, JSM-T20, Japan).

RESULTS AND DISCUSSION

Electrochemical Methods
Potentiodynamic polarization method: Figure 1 shows the anodic and cathodic Tafel polarization behavior of CS in 1M HCl solution in the absence and presence of varying doses of Pancuranium bromide at 298 K (similar curves are obtained in presence of Rocuronium bromide but not shown). From the diagram it is clear that both the cathodic reduction reaction and the anodic metal dissolution were inhibited when Pancuranium bromide and Rocuronium bromide were added to 1M HCl and this inhibition was more pronounced with increasing inhibitor concentration. The corrosion rate can be determined by Tafel extrapolation method [31, 32]. Table 2 reports the electrochemical parameters (i_{corr}, E_{corr}, β_a, β_c, C.R, θ and IE %) associated with polarization measurements of CS in 1M HCl solution in absence and presence of different concentrations of Pancuranium bromide and Rocuronium bromide. The results from Table 2 show that increasing the Pancuranium bromide and Rocuronium bromide doses leads to decreased in the corrosion current density (i_{corr}) and increased in IE, but the Tafel slopes (β_a , β_c) values are approximately constant indicating that Pancuranium bromide and Rocuronium bromide, as inhibitor functions through blocking the reaction sites on the metal surface without changing the anodic and cathodic reactions mechanism [33-35]. According to the E_{corr} values listed in table 2, indicate that the inhibitors, Pancuranium Bromide and Rocuronium Bromide, can be classified as mixed-type inhibitor.
The values (IE %) were calculated using the following equation (5) [36].

$$IE\% = 100 \times [\ (i^{°}_{corr} - i_{corr}) / i^{°}_{corr}] \tag{5}$$

Where $i^{°}_{corr}$ and i_{corr} are the corrosion current densities for uninhibited and inhibited solution, respectively.
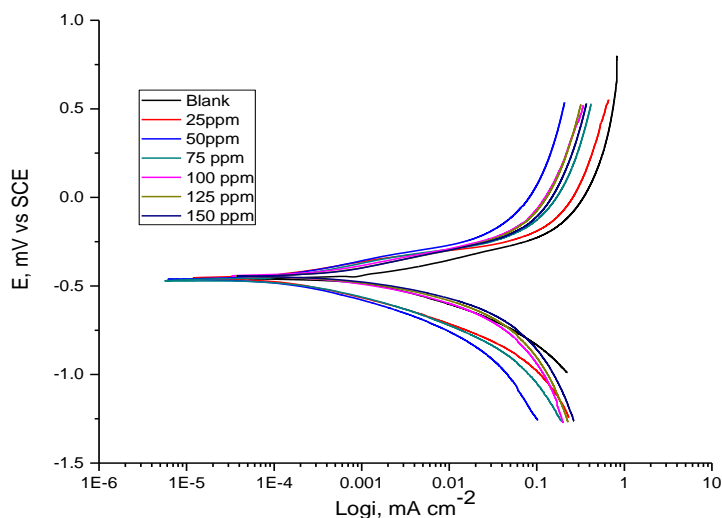
Figure 1. Potentiodynamic anodic and cathodic polarization curve of CS in 1M HCl solution with and without various doses of Pancuranium bromide at 298K

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Table 2. Electrochemical parameters (i_{corr}, E_{corr}, β_a, β_c, C.R, θ and IE%) associated with polarization measurements of CS in 1M HCl solution in absence and presence of different concentrations of Pancuranium bromide and Rocuronium bromide at 298 K

Inhibitors	Conc., ppm	-E_{corr}, mV (vs SCE)	$i_{corr.}$ (μA cm^{-2})	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R, mpy	θ	% IE
Blank	0.0	80	523	215	166	498	-----	-----
Pancuranium bromide	25	71	109.3	142	139	102.3	0.791	79.1
	50	63	100.9	151	118	98.4	0.807	80.7
	75	45	85.7	132	142	81.2	0.836	83.6
	100	51	66.9	149	131	63.3	0.872	87.2
	125	60	55.4	158	105	51.7	0.894	89.4
	150	38	42.8	160	158	39.1	0.918	91.8
Rocuronium bromide	25	62	157.9	169	160	152.3	0.698	69.8
	50	38	147	157	152	143.6	0.719	71.9
	75	53	123.4	161	133	120	0.764	76.4
	100	75	111.8	144	114	108.1	0.786	78.6
	125	69	98.8	136	140	95.7	0.811	81.1
	150	49	76.8	120	108	73.2	0.853	85.3

Electrochemical impedance spectroscopy (EIS) method: The effect of Pancuranium bromide dose on the impedance behavior of CS in 1M HCl solution at 25 ºC is presented in Figure 2. (similar curves are obtained in presence of the other inhibitor, Rocuronium bromide but not shown).The curves show a similar type of Nyquist plots for CS in the presence of various concentrations of inhibitor, Pancuranium bromide, the existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of drug molecules. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, and formation of porous layers and in homogenates of the electrode surface [37, 38]. The electrical equivalent circuit model is shown in Figure 3. It used to analyze the obtained impedance data. The model consists of the solution resistance (R_s), the charge-transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}). Excellent fit with this model was obtained with our experimental data. EIS data from Table 3 show that the R_{ct} values increases and the C_{dl} values decreases with increasing the Pancuranium bromide and Rocuronium bromide doses. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, decreasing the extent of dissolution reaction. The higher (R_{ct}) values, are generally associated with slower corroding system [39-40]. The (R_{ct}) values were used to calculate the (IE %) values through the following equation (6) :

$$IE\% = 100 \times \theta = 100 \times [R_{ct} - R^{\circ}_{ct} / R_{ct}] \qquad (6)$$

Where R_{ct} and R°_{ct} are the charge transfer resistances for inhibited and uninhibited solutions respectively. It is apparent that the IE increases with increasing the dose of the drug.
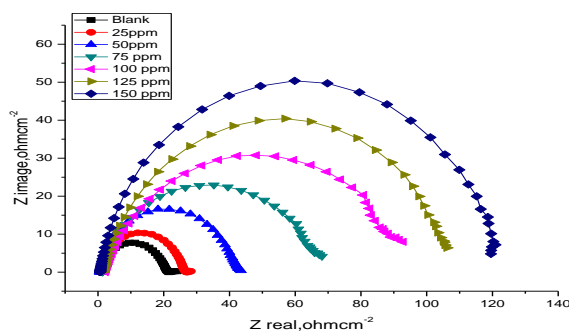
Figure 2. Impedance plots record for CS in 1M HCl solution with and without various doses of Pancuranium bromide at 298K and at respective corrosion potential.
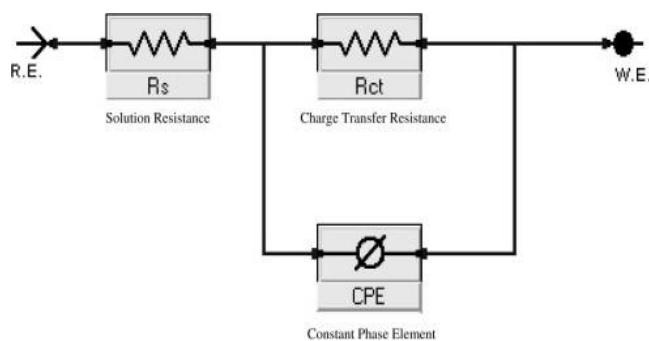
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Fig 3. Electrical equivalent circuit model used to fit the results of impedance

Table 3. Values of impedance parameter (R_{ct}, C_{dl}, θ and IE %) associated with impedance measurements of CS in 1M HCl solution in absence and presence of different doses of Pancuranium bromide and Rocuronium bromide, at 298K

Inhibitors	Conc., ppm	C_{dl}, μA cm^{-2}	R_{ct}, Ω cm^2	θ	%IE
Blank	0.0	95.3	23.1	----	----
Pancuranium bromide	25	92.6	30.7	0.247	24.7
	50	91.3	44.2	0.477	47.7
	75	89.5	70.2	0.670	67
	100	86.6	99.1	0.766	76.6
	125	83.0	113.5	0.796	79.6
	150	82.7	126.3	0.817	81.7
Rocuronium bromide	25	93.0	27.8	0.169	16.9
	50	94.2	42.5	0.456	45.6
	75	90.5	65.4	0.646	64.6
	100	88.6	85.2	0.728	72.8
	125	85.4	96.7	0.761	76.1
	150	83.9	111.3	0.792	79.2

From above results, the decrease in the C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer suggested that the inhibitor molecules function by adsorption at the metal/solution interface [41]. The (IE%) obtained from EIS measurements are close to those deduced from polarization measurements and confirm the results obtained from weight loss and indicate to Pancuranium Bromide and Rocuronium Bromide inhibitor is efficient inhibitor.

**Electrochemical Frequency Modulation Technique (EFM):**
Electrochemical frequency modulation (EFM) is nondestructive corrosion measurements technique that can directly give values of the corrosion current without prior knowledge of Tafel constant. Like EIS, it's a small signal ac technique unlike EIS, however two sine wave (at different frequencies) are applied to cell simultaneously. Because current is non-linear function of potential the system responds in non-linear way to potential excitation. The current response contains not only the input frequencies, but also contains frequency components which are the sum, difference and multiples of the two input frequencies. The two frequencies may not be chosen at random. They must both be small, integer multiples of a base frequency that determines the length of experiment. Figure 4 shows representative examples for inter modulation

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spectra obtain from EFM measurements for CS in 1M HCl solution with and without various concentrations of Pancuranium bromide at 298K and at respective corrosion potential (similar curves are obtained in presence of Rocuronium bromide but not shown). Each spectrum is a current response as a function of frequency. It is important to note that between the peaks the current response is very small. There is nearly noresponse (<100nA) at 4.5 Hz, for example, they are direct consequences of the EFM theory [42, 43]. Corrosion kinetic parameter such as inhibition efficiency (IE %), corrosion current density (i_{corr}), Tafel constants (β_a, β_c) and causality factors are listed in Table 4. are calculated from EFM technique. It's obvious that i_{corr}, values decrease while (IE %) increase with increase of Pancuranium bromide and Rocuronium bromide, concentration.IE% were calculated from equation (7):

$$IE\% = 100 \times \theta = 100 \times (1 - i_{corr} / i^{°}_{corr}) \tag{7}$$

Where $i^{°}_{corr}$ and i_{corr} are corrosion current density in the absence and presence of inhibitor, respectively. The great strength of EFM is causality factor which serve as an internal check on the validity of the EFM measurement. With the causality factors the experimental EFM data can be verified. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. It is quite obvious that the data obtained from chemical and electrochemical measurement were in good agreement with the result obtained from EFM.
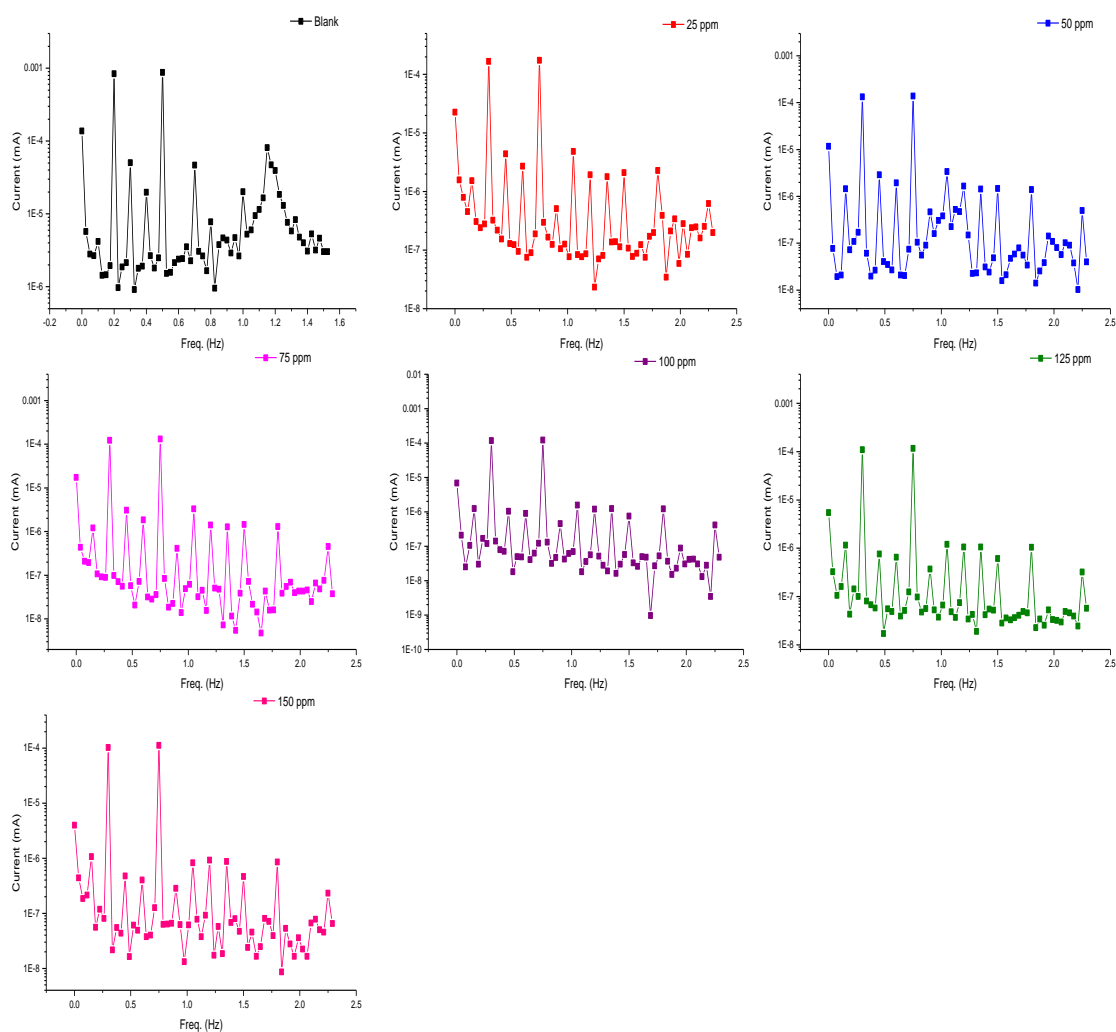

Figure 4.Intermodulation spectrum recorded for CS in 1M HCl solution with and without various doses of Pancuranium bromide at 298 K and at respective corrosion potential.

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Table 4. The electrochemical kinetic parameters obtained by EFM technique recorded for
CS electrode in 1M HCl solutions without and with various doses of
Pancuranium bromide and Rocuronium bromide at 298K

Inhibitor	Conc., ppm	i_{corr} µAcm^{-2}	β_c mVdec^{-1}	β_a mVdec^{-1}	CF-2	CF-3	CR mpy	θ	%IE
Blank	0.0	1420	85	116	2.4	3.1	592.1	-	-
Pancuranium bromide	25	279.1	124	125	1.9	3.3	130.1	0.803	80.3
	50	232.6	128	163	1.8	3.0	100.3	0.836	83.6
	75	214.4	121	119	1.9	2.9	98.5	0.850	85.0
	100	172.2	113	114	1.5	2.8	96.2	0.878	87.8
	125	143.7	124	125	1.4	3.6	94.9	0.898	89.8
	150	128.3	113	119	1.2	3.4	91.3	0.909	90.9
Rocuronium bromide	25	355.1	92	109	1.8	2.8	132.5	0.749	74.9
	50	285.1	141	147	1.2	3.3	104.2	0.799	79.9
	75	255.5	155	133	1.7	3.1	100. 5	0.820	82
	100	223.6	101	98	1.4	2.9	98.1	0.842	84.2
	125	178.2	148	134	1.8	3	96. 9	0.874	87.4
	150	149	135	125	1.6	2.6	94. 6	0.895	89.5

Chemical Technique: Weight loss (WL) of CS was determined at various time intervals in the absence and presence of different doses of Pancuranium bromide and Rocuronium bromide. Figure 5 shows the relation between corrosion rate and temperature for various doses of Pancuranium bromide (similar curves are obtained in presence of the other inhibitor, Rocuronium bromide but not shown). The calculated values of corrosion rate (k), surface coverage (θ) and inhibition efficiency (IE %) obtained from WL measurement for various doses of inhibitors in 1M HCl at 298-328 K are listed in table 5. It is evident from this table 5 that the corrosion rate of CS in 1M HCl increased by increasing the temperature and the (IE %) increased by increasing the concentration of inhibitors and on the other hand, decreased by increasing the temperature. The inhibition achieved by these compounds decreases in the following order: Pancuranium bromide > Rocuronium bromide
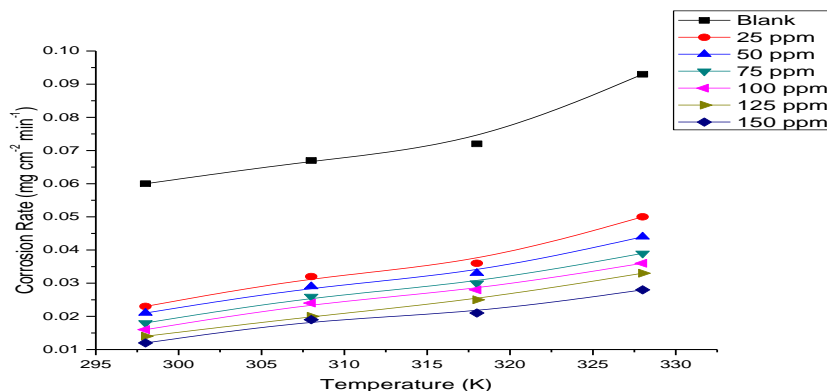
Figure 5. Relation between corrosion rate and temperature for various doses of Pancuranium bromide

Table 5. Variation of %IE of different inhibitors with their doses at 298 K from WL measurements at 120 min immersion in 1M HCl solution

Compound	Conc. ppm	Wt. loss mg/cm^{-2}	CR mg cm^{-2} min^{-1}	Θ	%IE
Blank	0.0	7.2	0.06	---	----
Pancuranium bromide	25	2.76	0.023	0.61	61
	50	2.52	0.021	0.65	65
	75	2.16	0.018	0.7	70
	100	1.92	0.016	0.73	73
	125	1.68	0.014	0.76	76
	150	1.44	0.012	0.8	80
Rocuronium bromide	25	3.62	0.03	0.49	49
	50	3.21	0.026	0.55	55
	75	2.71	0.022	0.62	62
	100	2.32	0.019	0.67	67
	125	1.98	0.016	0.72	72
	150	1.62	0.013	0.77	77

Effect of Temperature: The effect of temperature on the rate of corrosion of CS in 1M HCl containing different doses from investigated Pancuranium bromide and Rocuronium bromide, was tested by WL measurements over a temperature range from (298-328) K. The effect of increasing temperature on the corrosion rate (k) and (IE %) obtained from WL measurements. The relation between the corrosion rate (k) of CS and temperature (T) is often expressed by the Arrhenius equation (8) [31]:

$$\text{Log } k_{corr} = \log A - Ea^* / 2.303RT \qquad (8)$$

Where k, is the corrosion rate Ea*, is the apparent activation energy, R, is the universal gas constant, T is the absolute temperature and A is the frequency factor. the plot of log k against 1/T for CS corrosion 1M HCl in the absence and presence of different doses of Pancuranium bromide is represent in Figure 6. (similar curves are obtained in presence of the other inhibitor, Rocuronium bromide but not shown).
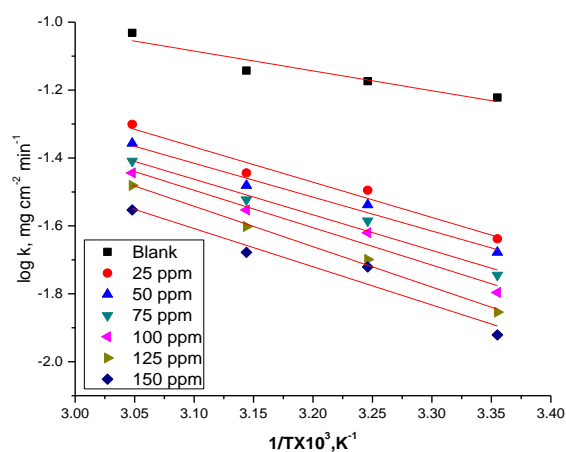
Figure 6. Arrhenius plots for CS corrosion in 1M HCl in the absence and presence of various doses of Pancuranium bromide

All parameters are given in Table 6. It is clear that the addition of Pancuranium bromide and Rocuronium bromide to acid solution increases the value of E_a^*. This mean that the adsorption of Pancuranium Bromide and Rocuronium Bromide on CS surface lead to formation of barrier layer that retard the metal activity in the electrochemical reactions of corrosion [44]. More desorption of Pancuranium bromide and Rocuronium bromide molecules at higher temperatures, the greater surface area of CS comes in contact with aggressive environment, resulting in an increase of corrosion rates with temperature. With high Pancuranium bromide and Rocuronium bromide concentration, this problem is avoided because decrease of surface coverage is close to saturation [45]. The increase in E_a^* after addition of Pancuranium bromide and Rocuronium bromide to 1M HCl solution can indicate the physical adsorption (electrostatic interaction) occurs in the first stage [46]. Enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the transition state theory Table 6.

$$Rate = (RT/Nh)\ exp\ (\Delta S^*/R)\ exp\ (-\Delta H^*/RT) \qquad (9)$$

where h is Planck's constant, N is Avogadro's number, ΔH^* and ΔS^* are the enthalpy and entropy change of activation. Figure 7 shows the plot of log (k/T) vs. 1/T for CS in 1M HCl in the absence and presence of different concentrations of inhibitor, Pancuranium Bromide (similar curves are obtained in presence of the other inhibitor, Rocuronium Bromide but not shown). Straight lines were obtained with slope of ($\Delta H^*/2.303\ R$) and an intercept of [log (R/Nh) + ($\Delta S^*/2.303\ R$)], from which the value of ΔH^* and ΔS^* were computed and are listed in Table 6.
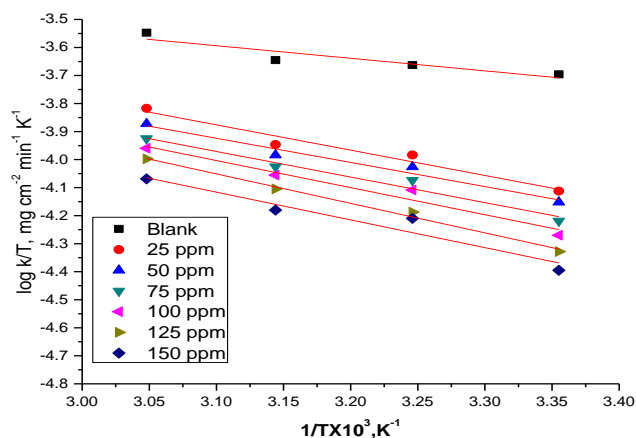
Figure 7. Transition state plot for CS corrosion in 1M HCl without and with various doses of Pancuranium bromide

Table 6. Thermodynamic activation parameters of the dissolution of CS in 1M HCl in the absence and presence of different doses of Pancuranium bromide and Rocuronium bromide

Inhibitor	Conc., Ppm	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
Blank	0.0	11.2	8.59	239.64
Pancuranium Bromide	25	18.9	17.28	222.11
	50	20.1	19.49	220.47
	75	23.1	20.45	216.38
	100	23.9	22.49	212.79
	125	24.8	25.14	209.58

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	150	27.5	27.0	205.53
Rocuronium Bromide	25	17.3	15.70	225.80
	50	19.6	17.0	222.30
	75	20.5	18.95	223.32
	100	22.5	21.0	218.40
	125	23.0	23.17	216.04
	150	26.1	24.53	211.72

The positive signs of ΔH^* reflect the endothermic nature of the CS dissolution process suggested that the dissolution of CS is slow [47]. Large and negative values of ΔS^* imply that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex [48].

Adsorption Isotherms: Adsorption of organic molecules at the metal/solution interface considers the first step in inhibition of metallic corrosion. That process depends on the molecule's chemical composition, temperature and electrochemical potential at the metal/solution interface. The adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, $Inh._{(sol.)}$, in the aqueous phase substitutes an "x" adsorbed on the metal surface.

$$Inh._{(sol.)} + xH_2O_{(ads.)} \rightarrow Inh._{(ads.)} + xH_2O_{(sol.)} \qquad (10)$$
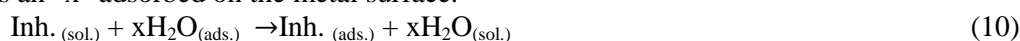
where x is known as the size ratio and simply equal the number of adsorbed water molecules replaced by a single inhibitor molecule. Basic information on the interaction between the inhibitor of CS surface can be provided by the adsorption isotherms. In order to obtain the best isotherm, the relation between degree of surface coverage (θ) and inhibitor concentration (C) at different temperatures must be found. by far the results of investigated inhibitor were best fitted by Temkin adsorption isotherm.

Figure 8 shows the plotting of (θ) against (log C) at different temperature for investigated Pancuranium bromide (similar curves are obtained in presence of the other inhibitor, Rocuronium bromide but not shown). The plot gave straight lines with nearly unity slope indicating that the adsorption of investigated compound on CS surface follows Temkin adsorption isotherm [49]. The correlation (R^2) was used to determine the best fit isotherm which was obtained for Temkin as shown in Table 7. According to this isotherm, θ, is related to the equilibrium constant (K_{ads}) by the following equation (11):

$$\Theta_{coverage} = (2.303 / a) \, Log \, K_{ads} + (2.303 / a) \, Log \, C \qquad (11)$$

Where θ is the degree of surface coverage [θ = %IE/100], K_{ads} is the adsorption equilibrium constant, C is the concentration (mol L^{-1}) of the inhibitor and "a" (heterogeneous factor of metal surface) is a molecular interaction parameter depending upon molecular interactions. A plot of θ versus Log C should give straight lines with slope equals (2.303/a) and the intercept is (2.303/a) Log K_{ads} and K_{ads} is the adsorption equilibrium constant related to the Gibbs free energy of adsorption ΔG_{ads} as [50]:

$$K_{ads} = 1/ 55.5 \, exp. \, (-\Delta G_{ads}/ RT) \qquad (12)$$

Where R is the universal gas constant, T is the absolute temperature. The value 55.5 is the concentration of water on the metal surfaces in molar value of K_{ads} and ΔG^o_{ads}. For Pancuranium Bromide and Rocuronium Bromide as inhibitors were calculated and are recorded in Table 7. The high values of K_{ads} for studied inhibitors indicate stronger adsorption on the CS surface in 1M HCl solution. This can be explained by presence of heteroatom and π-electrons in the Pancuranium Bromide and Rocuronium Bromide molecules. The stronger and more stable the adsorbed layer of the studied inhibitor on the metal surface and consequently, the higher the inhibition efficiency [51]. This data supports the good performance of Pancuranium Bromide and Rocuronium Bromide as inhibitors for CS in 1M HCl solution. The negative

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value of $\Delta G°_{ads}$, are consistent with the spontaneity of the adsorption process and the stability of adsorbed layer on the steel surface. Generally, the values of $\Delta G°_{ads}$ up to -20 kJ mol^{-1} are consistent with physisorption, while those around - 40 kJmol^{-1} or higher are associated with chemisorption as a result of sharing or transfer of electrons from organic molecule to metal surface to form coordination bond [52]. In the present study, the calculated values of $\Delta G°_{ads}$ obtained in range -43 and -47.2 kJ mol^{-1}. Table 7 indicates that the adsorption of mechanism of Pancuranium bromide and Rocuronium bromide on CS in 1M HCl solution at studied temperatures may be combination of both physisorption and chemisorption. (Comprehensive adsorption) [53]. However the physisorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism.
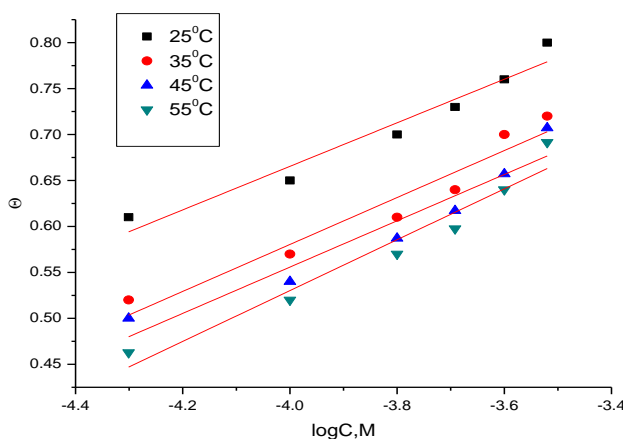

Figure 8. Temkin adsorption plots for CS in the presence of Pancuranium bromide

Table 7. Shows some parameters obtained from Temkin adsorption isotherm for CS in 1M HCl in the presence of Pancuranium bromide and Rocuronium bromide

Inhibitors	Temp, K	Log K_{ads}, M^{-1}	a	$-\Delta G°_{ads.}$ kJ mol^{-1}	$-\Delta H°_{ads.}$ kJ mol^{-1}	$-\Delta S°_{ads.}$ Jmol^{-1} k^{-1}	R^2
Pancuranium bromide	298	6.1453	9.7	45.0	72	163.5	0.961
	308	5.738	9.0	44.1			0.952
	318	5.1386	9.1	41.9			0.924
	328	4.578	8.3	39.7			0.966
Rocuronium bromide	298	5.677	8.5	42.3	67	181.1	0.940
	308	5.252	9.2	41.2			0.938
	318	4.8963	9.6	40.4			0.949
	328	4.1512	9.4	37.0			0.915

Quantum chemical calculations: Quantum chemical calculations have proved to be very powerful tool for studying corrosion inhibition mechanism [54]. Figure 9 represents the molecular orbital plots and Mulliken charges of investigated Pancuranium bromide and Rocuronium bromide; Theoretical calculations were performed for only the neutral forms, in order to give farther insight into the experimental results. Values of quantum chemical indices such as energies of lowest unoccupied molecular orbitals (LUMO) and energy of highest occupied molecular orbitals (HOMO) (E_{HOMO} and E_{LUMO}), the formation heat ΔH

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and energy gap ΔE, are calculated by semi empirical AMI, MNDO and PM3 methods has been given in Table 8. It has been reported that the higher or less negative E_{HOMO} associated with inhibitor, the greater the tendency of offering electrons to unoccupied d̲ orbital of the metal, and the higher the corrosion IE [55] in addition, the lower E_{LUMO}, the easier the acceptance of electrons from metal surface [56]. As known, a hard molecule has a large energy gap, and a soft molecule has a small energy gap. Soft molecules are more reactive than hard molecules, in general. The energy gap between the HOMO and LUMO energy levels of the molecules is an important factor that should be considered. A low ΔE facilitates adsorption of the molecule [57] and thus will cause higher IE.
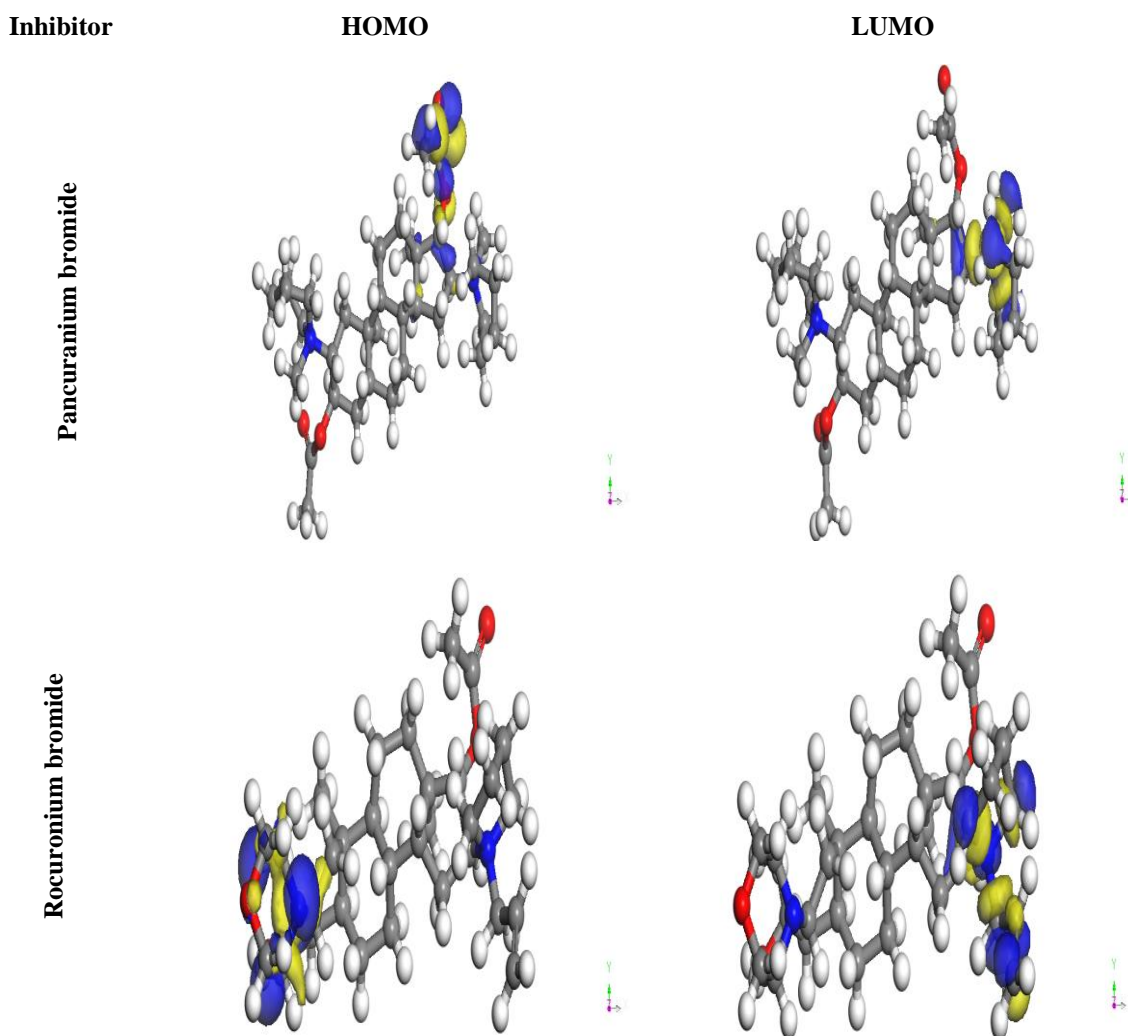
	HOMO	**LUMO**
Inhibitor		

Figure 9. Molecular orbital plots of Pancuranium bromide and Rocuronium bromide

Table 8. Calculated quantum chemical properties for Pancuranium bromide and Rocuronium bromide

Compound	$-E_{HOMO}$ (ev)	$-E_{LUMO}$ (ev)	$\Delta E = E_{LUMO} - E_{HOMO}$ (ev)	$\eta = \Delta E /2$ (ev)	$\sigma = 1/ \eta$ (ev^{-1})	$Pi = (E_{HOMO} + E_{LUMO})/2$ (ev)	$X = - pi$ (ev)	Dipole moment (Debye)
Pancuranium bromide	10.564	3.947	6.617	3.309	0.302	-7.256	7.256	17.694
Rocuronium bromide	15.655	5.386	10.269	5.135	0.195	-10.521	10.521	6.647

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From Table 8, it is clear that the ΔE value obtained in case of Rocuronium bromide, is higher than that value of Pancuranium Bromide, which enhance the assumption that Pancuranium Bromide molecule as inhibitor will absorb by strong way on CS surface, due to facilitating of electron transfer between molecular orbital HOMO and LUMO which takes place during its adsorption on the metal surface and therefore maximum IE will occurred. Also it can be seen that the low value of E_{HOMO} facilitates the adsorption and the inhibition by supporting the transport process through the adsorbed layer. According to reports, excellent corrosion inhibitors are usually those organic compounds who are not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [58]. It can be seen that all calculated quantum chemical parameters validate these experimental results. From the results of E_{HOMO}, E_{LUMO} and energy gap (ΔE) the order of IE is as follows: Pancuranium bromide > Rocuronium bromide.

Scanning Electron Microscopy (SEM) Studies: Figure 10A-D represents the SEM micrographs obtained of CS surface of pure metal and after exposure to 1M HCl solution for 24 h immersion with and without addition of 150 ppm of Pancuranium bromide and Rocuronium bromide. It is clear that CS surfaces after exposure to 1M HCl solution in absence of Pancuranium bromide and Rocuronium bromide suffer from severe corrosion attack as shown in Figure10B. On the other hand, the morphology of CS surface is quite different from the previous one when the Pancuranium bromide and Rocuronium bromide are in the solution as shown in Figures10 C & D where almost not affected by acid corrosion.
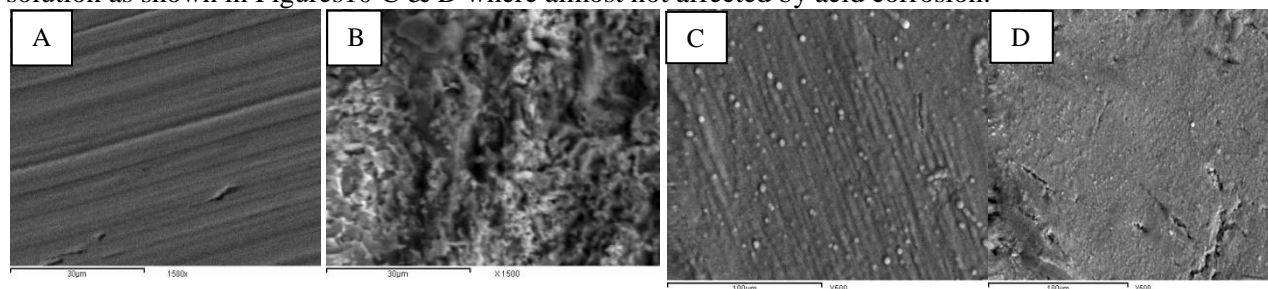
Figure 10. SEM micrographs of A: CS pure; B: CS dipped in 1M HCl solution in absence of drugs; C: CS dipped in 1M HCl solution after 24 h immersion in in 1M HCl with 150 ppm Pancuranium bromide; D: CS dipped in 1M HCl solution after 24 h immersion in in 1M HCl with 150 ppm Rocuronium bromide all at 298K

Inhibition Mode of Action: We noted the formation of a film which is distributed in a random way on the whole surface of the CS. Due to the adsorption of the Pancuranium bromide and Rocuronium bromide on the CS that block the active site present on the CS surfaces. These compounds can be adsorbed on the metal surface through the lone pair of electrons of nitrogen, oxygen atoms and delocalized π–electrons of heterocyclic ring. The difference in IE of these investigated compounds can be explained on the basis of their molecular structures. Pancuranium bromide Contains eight active centers (4 O atoms, 2 N atoms and 2 Br atoms) and this compound lies flat on the CS surface, so, more surface area was covered and hence, more IE was observed. Rocuronium bromide comes after Pancuranium bromide in IE because it contains seven active centers (4 O atoms, 2 N atoms and one Br atom) covers less surface area than Pancuranium bromide, hence it has less IE. So, it comes after Pancuranium bromide in. In addition to the above the Pancuranium bromide has higher molecular size 732.6699 g mol^{-1} than Rocuronium bromide 609.6782 g mol^{-1}, so more surface area was covered and hence, more IE was obtained. On another hand the involvement of inhibitor molecules in the interaction with the reaction active sites of CS surface, lead to a decrease in the contact between CS and the aggressive medium, 1M HCl, and hence exhibited excellent inhibition effect [59].

CONCLUSIONS

The tested Pancuranium bromide and Rocuronium bromide establish a very good inhibition for CS corrosion in HCl solution, where IE % increased by increasing in Pancuranium bromide and Rocuronium bromide dose. The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed Pancuranium bromide and Rocuronium bromide molecules takes place. Pancuranium bromide and Rocuronium bromide inhibit CS corrosion by adsorption on its surface and follow Temkin adsorption isotherm. Polarization curves showed that Pancuranium bromide and Rocuronium bromide are mixed-type inhibitors. Double layer capacitance (C_{dl}) decreases with increasing the inhibitor dose added. While the charge-transfer resistance (R_{ct}) increases. The values of IE obtained from the different techniques used are Compatible with each other. From different techniques used in this study the order of IE is as the follows: Pancuranium bromide > Rocuronium bromide.

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