Corrosion Protection of C-Steel in Hydrochloric Acid Solutions Using Flaxedil (Gallamine Triethiodide) Drug

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ABSTRACT

The inhibiting effect of Flaxedil (FD) as corrosion inhibitor of carbon steel (CS) in 1 M HCl was studied by gravimetric technique (GT), potentiodynamic polarization (PP), electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) measurements. Polarization curves showed that Flaxedil behaved as mixed-type inhibitor. The adsorption isotherm of Flaxedil on the CS surface follows Temkin adsorption isotherm. Some thermodynamic parameters were calculated and discussed. The results indicated that the inhibition efficiency increases with increasing the dose of the drug, while decreases with increasing the temperature. Some quantum chemical parameters and the Mulliken charge densities for Flaxedil were calculated by the semi-empirical AM1 method to provide further insight into the mechanism of inhibition of the corrosion process. The results obtained from chemical and electrochemical techniques are in good agreement.

Graphical Abstract
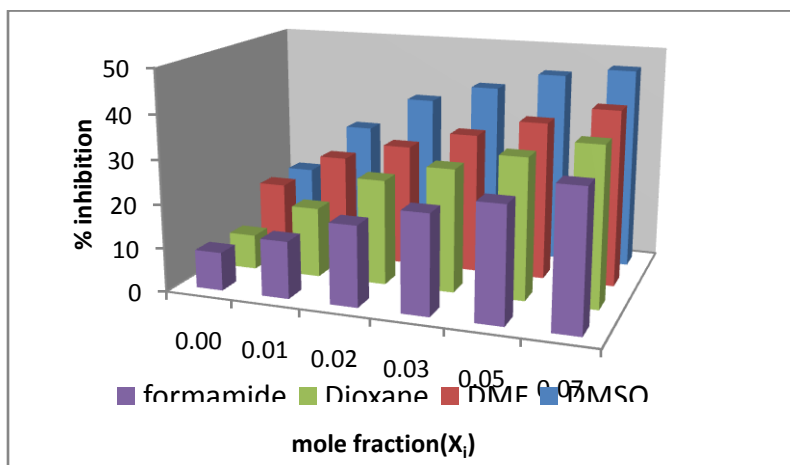
Keywords: Carbon steel, Corrosion inhibition, EIS, SEM, EFM, Flaxedil, HCl .

INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, the use of inhibitors is one of the best options of protecting metals and alloys against corrosion, especially in acidic media [1]. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having hetero atoms in their aromatic or long- chain carbon system. However, most of these inhibitors are toxic to the environment containing heavy metals. This has prompted the search for green corrosion inhibitors [2]. Most of organic inhibitors are expensive, toxic and have negative effect on the environment these properties restrict its use to inhibit the metal corrosion. Thus it is important and necessary to develop low cost and environmentally safe corrosion inhibitors [3-4]. In the recent year's drugs has been used as corrosion inhibitors. According to Eddy and Odoemelam, the use of drugs for the inhibition of the corrosion of metals has some advantages over the use of some organic/inorganic inhibitors because of their eco- environmental nature [5]. Drugs are nontoxic, cheap, negligible negative effects on environment, so it suggested replacing the traditional toxic corrosion inhibitors [6]. Many authors generally agree that drugs are inhibitors that can compete favorably with green corrosion inhibitors and that most drugs can be synthesized from natural products. The choice of some drugs used as corrosion inhibitors is based on the following: (a) drug molecules contain oxygen, nitrogen and Sulphur as active centers, (b) drugs are reportedly environmentally friendly and important in biological reactions and (c) drugs can be easily produced and purified [7-11]. The inhibition action of these drugs was attributed to blocking the surface via formation of insoluble complexes on the metal surface. Which markedly change the corrosion- resisting property of the metal [12-13]. And so the study of the relations between the adsorption and corrosion inhibition is of great important. Heterocyclic compounds have shown high inhibition efficiency for iron in both HCl [14] and H_2SO_4 solutions [15]. As a Gallamine triethiodide , Flaxedil have rarely been studied as inhibitor for CS in HCl solution. For this reason, the objective of the present study is to investigate the inhibiting action of a Flaxedil as Gallamine triethiodide in 1M HCl solution at (298-328 K) using different techniques.

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 drug (Flaxedil), has been investigated and purchased from Sanofi-Aventis pharmaceutical company, Cairo, Egypt.
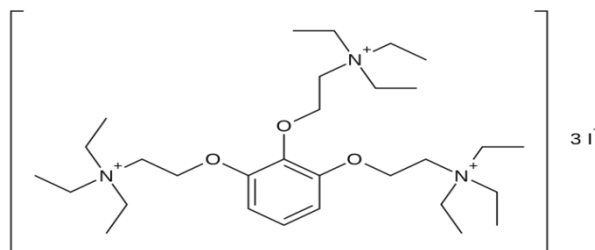
2-[2,3-bis[2-(triethylazaniumyl)ethoxy]phenoxy]ethyl-triethylazanium;triiodide
$C_{30}H_{60}N_3O_3^{+3} \cdot 3\ I^-$, 891.529 g mol^{-1}

Solutions: The stock solution of the aggressive medium (6 M HCl), was prepared by dilution of analytical grade (37%) HCl with bi-distilled water and checked by titration with standard solution of Na_2CO_3. 1 M HCl was prepared by dilution by bi-distilled water. The dose ranges of the inhibitor used was 25-150 ppm.
Chemical Methods: Six parallel CS sheets of $2.0 \times 2.0 \times 2$ cm were abraded with various grades 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, contained 150 mL of HCl with and without addition of different doses of investigated drug as inhibitor. Through period time 30 min. take out coupons, washed, dried and re-weighted accurately through 3h at various temperatures from 298 to 328 K [16]. The average WL of six parallel CS sheets could be obtained. The IE% and the degree of surface coverage, (θ) was calculated as follows using eq. (1) [17]:

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

Where, W° and W are the values of the average WLs without and with addition of the drug, respectively. Corrosion rate was calculated using eq. (2):

$$\text{Corrosion Rate } (k_{corr}) = W/A \times T \tag{2}$$

Where, W is weight loss at certain time (t) in min. and (A) area in cm^2 [18].

Electrochemical Techniques: Electrochemical experiments were carried out using cell consists of three electrodes (a) Working electrode (WE) is CS sheet 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 [19] (b) Reference electrode is saturated calomel electrode (SCE), used directly in contact with working solution, while all potential value was recorded against SCE. Lugging-Haber capillary tube was also included in the design, Lugging capillary tip is made very close to the surface of the WE to minimize IR drop [20] (c) Platinum foil (1cm^2) as auxiliary electrode. All electrochemical measurements were performed in solution 1M HCl with and without various doses of Flaxedil at 298 K under unstirred 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 methods
(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 the following eq.:

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

Where, R°_{ct} and R_{ct} are the charge transfer resistances without and with of the drug, respectively [21].
(b) EFM measurements were carried out using two frequency 2 and 5 Hz. The base frequency was 0.1 Hz. 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 [22].

Destructive method: This method includes DC PP technique which was used to determine i_{corr} under steady state conditions by applying potential from -1500 to +500 mV to obtain Tafel polarization curves and the result current is plotted as logarithm scale vs potential related to SCE, extrapolating of two Tafel regions give ($i_{corr.}$) and ($E_{corr.}$). The rate of corrosion (k_{corr}) = 0.13($i_{corr.}$) (Equivalent weight) / D. where, D is density in g/cm^3 [23]. Eq. (4) was used to determine IE% and (θ):

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

Where i_{corr} and i°_{corr} are the corrosion current densities without and with Flaxedil, respectively.

Surface examination: The CS surface was prepared by keeping the coupons for 24 h in 1M HCl with and without Flaxedil, 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 desiccator without any further treatment. The corroded CS were examined using an X-ray diffractometer Philips (pw-1390) with Cu-tube (Cu Ka1, I=1.5405A°), scanning electron microscope (SEM, JSM-T20, Japan).

RESULTS AND DISCUSSION

Weight loss Technique (GT): Weight loss (WL) of CS was determined at various time intervals without and with different doses of Flaxedil. Figure 1 shows the WL-time curves for CS in 1M HCl without and with various doses of Flaxedil at 298 K. This Figure shows that the curves in the presence of Flaxedil fall significantly below that of free HCl. The calculated values of (k_{corr}), (θ) and (IE %) obtained from WL measurement for various doses of Flaxedil in 1M HCl at 298-328 K is listed in Table 1

Table 1. Calculated values of (k_{corr}) and (IE %) for CS in 1M HCl without and with Flaxedil at 298-328 K

Conc. ppm	(k_{corr}) mg cm^{-2} min^{-1}				IE %			
	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K
Blank	0.06	0.067	0.072	0.093	---	---	---	---
25	0.022	0.028	0.033	0.047	62	58	54	49
50	0.018	0.025	0.031	0.043	69	63	57	54
75	0.016	0.021	0.028	0.040	72	69	61	57
100	0.014	0.017	0.025	0.034	75	74	65	63
125	0.013	0.015	0.023	0.030	78	77	68	68
150	0.011	0.013	0.020	0.027	81	80	72	71

It is evident from this Table 1 that the k_{corr} increased by increasing the temperature and the (IE %) increased by increasing the dose of Flaxedil and on the other hand, decreased by increasing the temperature.

Effect of temperature: The effect of temperature on the rate of corrosion of CS in 1M HCl containing different doses from investigated inhibitor, Flaxedil, was tested by weight loss measurements over a temperature range from (298:328) K. Relation between k_{corr} and T for various doses of the Flaxedil is shown in figure 2.The effect of increasing temperature on the corrosion rate (k) and (IE %) obtained from weight loss measurements. The relation between the corrosion rate (k) of CS and temperature (T) is often expressed by the Arrhenius equation (5) [24].

$$\text{Log } k_{corr} = \log A - E^{*}_{a} / 2.303RT \qquad (5)$$

Where k, is the corrosion rate E^{*}_{a}, 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 Flaxedil is representing in Figure 3.

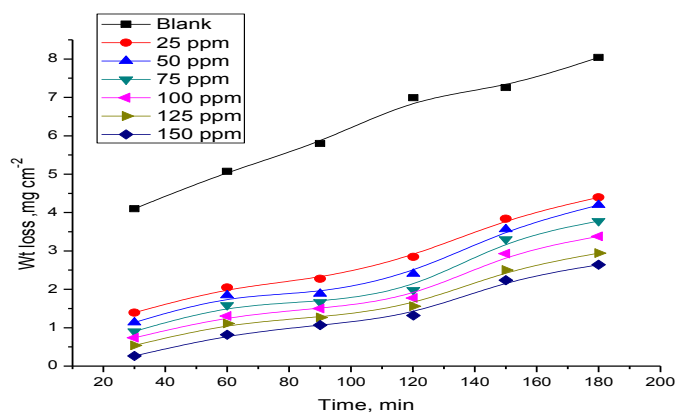**Fig 1.** WL-time curves for the corrosion of CS in 1M HCl without and
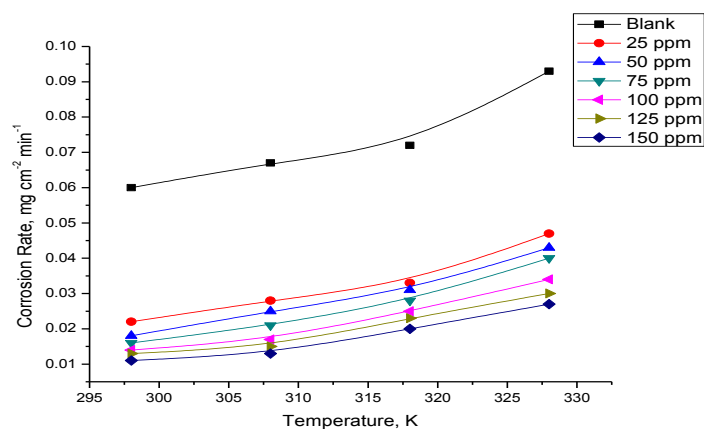with various doses of Flaxedil at 298 K

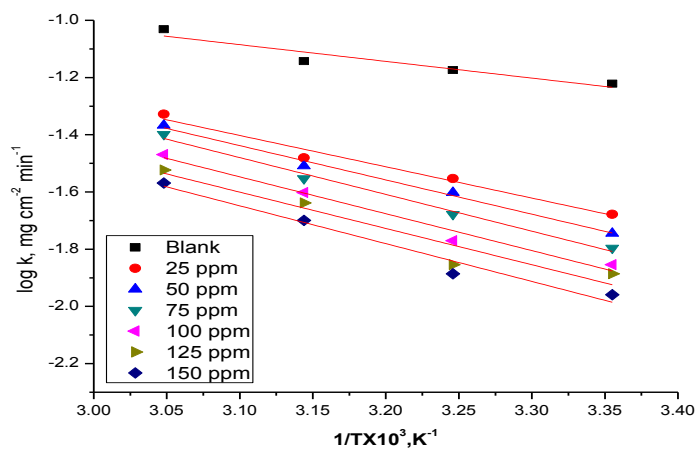**Fig 2.** Relation between k_{corr} and T for various doses of the Flaxedil

Fig 3. Arrhenius plots for CS corrosion in 1M HCl without and with various doses of Flaxedil

723

It is clear that the addition of Flaxedil to acid solution increases the value of E_a^*. This means that the adsorption of Flaxedil on CS surface lead to formation of barrier layer that retard the metal activity in the electrochemical reactions of corrosion [25]. More desorption of Flaxedil 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 Flaxedil dose, this problem is avoided because decrease of surface coverage is close to saturation [26] the increase in E_a^* after addition of Flaxedil to 1M HCl solution can indicate the physical adsorption (electrostatic interaction) occurs in the first stage [27]. Enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the transition state theory.

$$k_{corr} = (RT/ Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \tag{6}$$

Where h is Planck's constant, N is Avogadro's number, ΔH^* and ΔS^* are the enthalpy and entropy change of activation. Figure 4 shows the plot of log (k/T) vs. 1/T for CS in 1M HCl in the absence and presence of different doses of various dose of inhibitor, Flaxedil. 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 3.
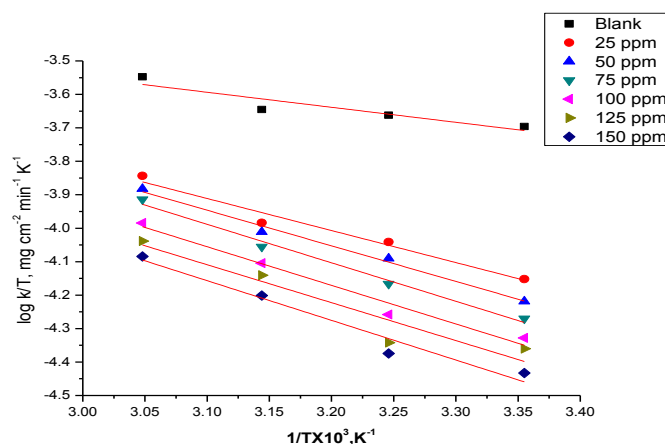

Fig 4. Transition state plots for CS corrosion in 1M HCl without and with various doses of Flaxedil

Table 3. Thermodynamic activation parameters of the dissolution of CS in 1M HCl without and with different doses of Flaxedil

[inhibitor] ppm	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
Blank	11.2	8.6	239.6
25	20.9	18.3	215.5
50	22.9	20.4	209.9
75	24.6	22.0	205.6
100	25.7	24.1	206.6
125	27.3	26.7	203.9
150	30.3	29.8	198.6

The positive signs of ΔH^* reflect the endothermic nature of the CS dissolution process suggested that the dissolution of CS is slow [28]. 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 [29].

Adsorption isotherms: Adsorption of organic molecule, at the metal/solution interface consider the first step in inhibition of metallic corrosion. This 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. $_{(sol.)}$ + xH2O$_{(ads.)}$ → Inh. $_{(ads.)}$ + xH2O$_{(sol.)}$ (7)
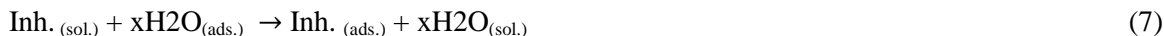
Where x is known as the size ratio and simply equal the number of adsorbed water molecules replaced by a single inhibitor molecule. Basic information on the interaction between the inhibitor of CS surface can be provided by the adsorption isotherms. In order to obtain the best isotherm, the relation between degree of surface coverage (θ) and inhibitor dose (C) at different temperatures must be found. By far the results of investigated inhibitor were best fitted by Temkin adsorption isotherm. Figure 5 show the plotting of (θ) against (log C) at different temperature for investigated inhibitor, Flaxedil, the plot gave straight lines with nearly unity slope indicating that the adsorption of investigated compound on CS surface follows Temkin adsorption isotherm [30].

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

Where C is the dose of inhibitor, θ the fractional surface coverage and K_{ads} is the adsorption equilibrium constant related to the Gibbs free energy of adsorption ΔG^{o}_{ads} as [31]:

$K_{ads} = 1/ 55.5 \exp (-\Delta G^{o}_{ads}/ RT)$ (9)

Where the value 55.5 is the dose of water on the metal surface. The value of K_{ads} and ΔG^{o}_{ads} for Flaxedil as inhibitor were calculated and are recorded in Table 4. The high values of K_{ads} for studied inhibitor indicate stronger adsorption on the CS surface in 1M HCl solution. This can be explained by presence of heteroatom and π-electrons in the Flaxedil molecules. The stronger and more stable the adsorbed layer of the studied inhibitor on the metal surface and consequently, the higher the IE [32]. This data support the good performance of Flaxedil as inhibitor for CS in 1M HCl solution. The negative values 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 $\Delta G^{°}_{ads}$ upto -20 kJ mol^{-1} are consistent with physisorption, while those around - 40 kJ mol^{-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 [33]. In the present study, the calculated values of $\Delta G^{°}_{ads}$ obtained in range -43 and -47.2 kJ mol^{-1}. Table 4 indicates that the adsorption mechanism of Flaxedil on CS in 1M HCl solution at studied temperatures may be combination of both physisorption and chemisorption. (Comprehensive adsorption) [34]. However the physisorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism.
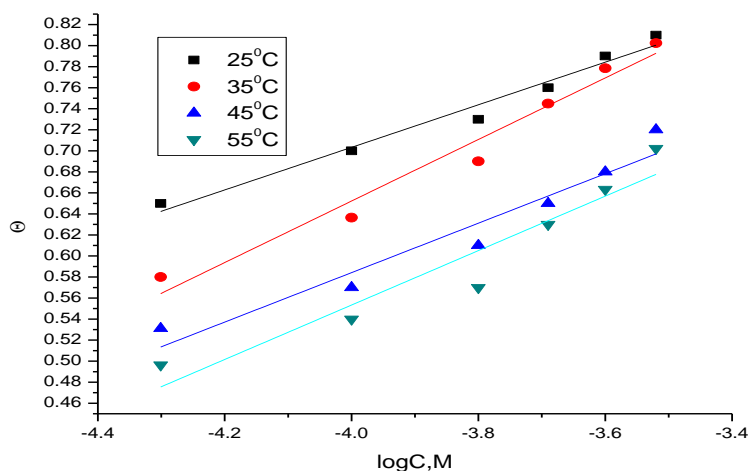

Fig 5. Temkin adsorption plots for CS in the presence of Flaxedil

Table 4. Shows some parameters obtained from Temkin adsorption isotherm for CS in 1M HCl in the presence of Flaxedil

Temp, K	Log K_{ads}, M^{-1}	a	$-\Delta G°_{ads}$, kJ mol^{-1}	$-\Delta H°_{ads}$, kJ mol^{-1}	$-\Delta S°_{ads}$, J mol^{-1} k^{-1}	R^2
11.3	6.5415		47.2			0.970
7.8	5.975		45.5			0.962
318	5.7868	9.7	45.8	84.0	123.2	0.942
328	5.1139	8.8	43.0			0.937

Electrochemical Methods

Potentiodynamic polarization technique: Figure 6 shows the anodic and cathodic Tafel polarization behavior of CS in 1M HCl solution in the absence and presence of varying doses of inhibitor, Flaxedil at 298 K. From the diagram it is clear that both the cathodic H_2 reduction reactions and the anodic metal dissolution were inhibited when investigated inhibitor, Flaxedil, were added to 1M HCl and this inhibition was more pronounced with increasing inhibitor dose. The corrosion rate can be determined by Tafel extrapolation method [35].
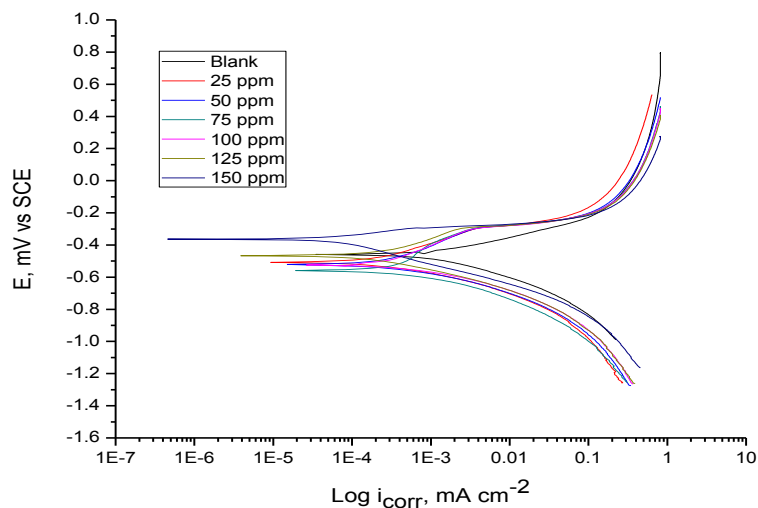

Fig 6. Potentiodynamic anodic and cathodic polarization curve of CS electrode in 1M HCl solution with and without various doses of inhibitor, Flaxedil, at 298 K

Table 5 shows 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 doses of Flaxedil. The results from Table 5 showed that increasing the inhibitor, Flaxedil, dose leads to decrease in the corrosion current density (i_{corr}) and increased in inhibition efficiency, but the Tafel slopes (β_a, β_c), values are approximately constant indicating that Flaxedil, as inhibitor functions through blocking the reaction sites on the metal surface without changing the anodic and cathodic reactions mechanism [36]. According to the E_{corr} values listed in table 5, indicate that the inhibitor, Flaxedil, can be classified as mixed-type inhibitor.

The IE% values were calculated using the following equation (10) [37].

$$IE\% = 100 \times [(i°_{corr} - i_{corr}) / i°_{corr}] \tag{10}$$

Where $i°_{corr}$ and i_{corr} are the corrosion current densities for uninhibited and inhibited solution, respectively. Table 5 shows that the IE% increases with increasing inhibitor dose.
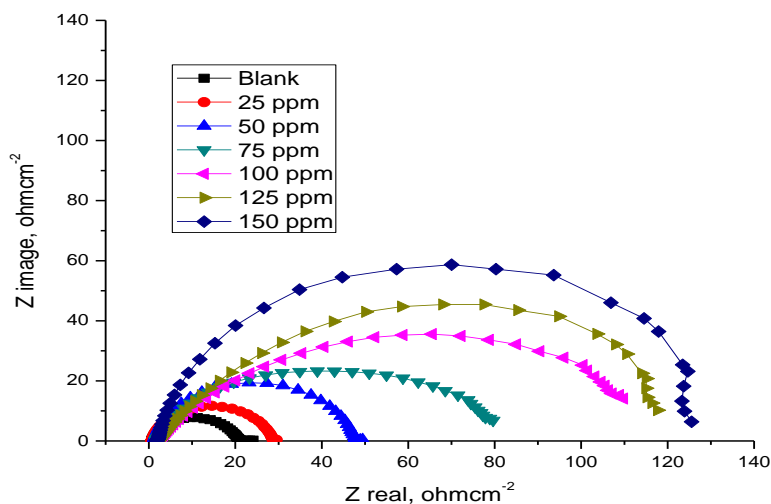
Table 5. Electrochemical parameters (i_{corr}, E_{corr}, β_a, β_c, C.R, θ and IE%) associated with polarization measurements of CS in 1M HCl solution in absence and presence of different doses of inhibitor, Flaxedil, at 298 K

| Conc., ppm	-E_{corr}, mV vs SCE	$i_{corr.}$ $\mu A\ cm^{-2}$	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R, mpy	Θ	% IE
0.0	80	523	215	166	498	-----	-----
25	77	97.8	123	117	94.3	0.813	81.3
50	60	78.9	134	149	74.1	0.849	84.9
75	53	56.4	169	127	54.4	0.892	89.2
100	32	44.4	144	119	41.9	0.915	91.5
125	21	32.9	152	157	29.4	0.937	93.7
150	18	26.6	116	123	23.8	0.949	94.9

EIS tests: The effect of inhibitor, Flaxedil, dose on the impedance behavior of CS in 1M HCl solution at 298 K is presented in Figure 7. The curves show a similar type of Nyquist plots for CS in the presence of various doses of inhibitor, Flaxedil, the existence of single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor 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 [38]. The electrical equivalent circuit model is shown in Figure 8. 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 6 showed that the R_{ct} values increases and the C_{dl} values decreases with increasing the inhibitor, Flaxedil, 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]. The (R_{ct}) values were used to calculate the (IE %) values through the following equation (11):

$$IE\% = 100 \times \theta = 100 \times [\ R_{ct} - R^{°}_{ct} / R_{ct}] \qquad (11)$$

Where R_{ct} and $R^{°}_{ct}$ are the charge transfer resistance for inhibited and uninhibited solutions. It is apparent that the inhibition efficiency increases with increasing dose of inhibitor.

Fig. 7 Impedance plots recorded for CS in 1M HCl solution with and without various doses of Flaxedil at 298 K
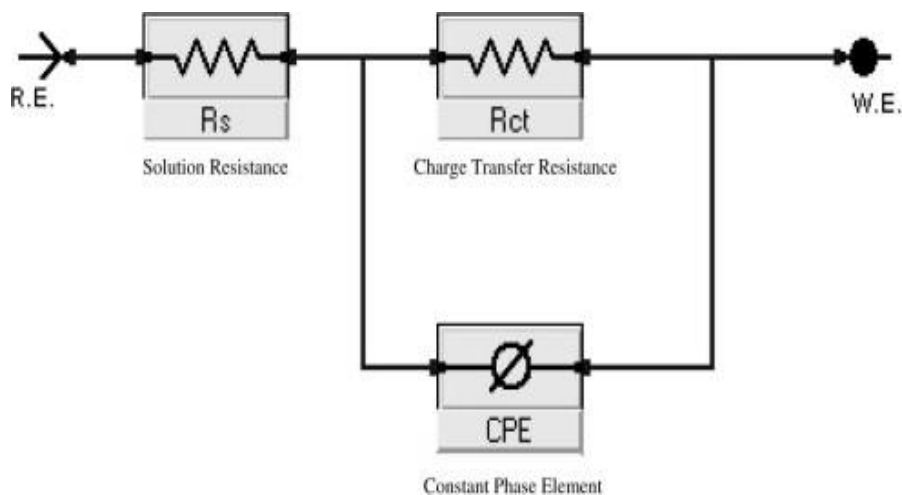
Fig 8. Electrical equivalent circuit model used to fit the results of impedance

Table 6. 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 inhibitor, Flaxedil, at 298 K

Conc., ppm	C_{dl}, μA cm^{-2}	R_{ct}, Ω cm^2	θ	% IE
0.0	95.3	23.1	----	----
25	91.7	33.5	0.310	31
50	89.4	52.7	0.561	56.1
75	87.3	87.2	0.735	73.5
100	85.4	120.4	0.808	80.8
125	82.1	128.1	0.819	81.9
150	81.3	137.2	0.831	83.1

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 [40]. The (IE%) obtained from EIS measurements are close to those deduced from polarization measurements and confirmed the results obtained from weight loss and indicate to Flaxedil inhibitor is efficient inhibitor.

EFM tests: Electrochemical frequency modulation (EFM) is nondestructive corrosion measurements technique that can directly give values of the corrosion current without period knowledge of Tafel constant. Figure 9 shows representative examples for intermodulation spectra obtain from EFM measurements for CS electrode in 1M HCl solution with and without various doses of Flaxedil at 298 K. Table 7 shows corrosion kinetic parameters such as inhibition efficiency (IE %), corrosion current density (i_{corr}), Tafel constants (β_a, β_c) and causality factors which calculated from EFM technique. It's obvious that i_{corr}, values decrease while (IE %) increase with increase of Flaxedil dose. IE% and θ were calculated from eq. (10). 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.
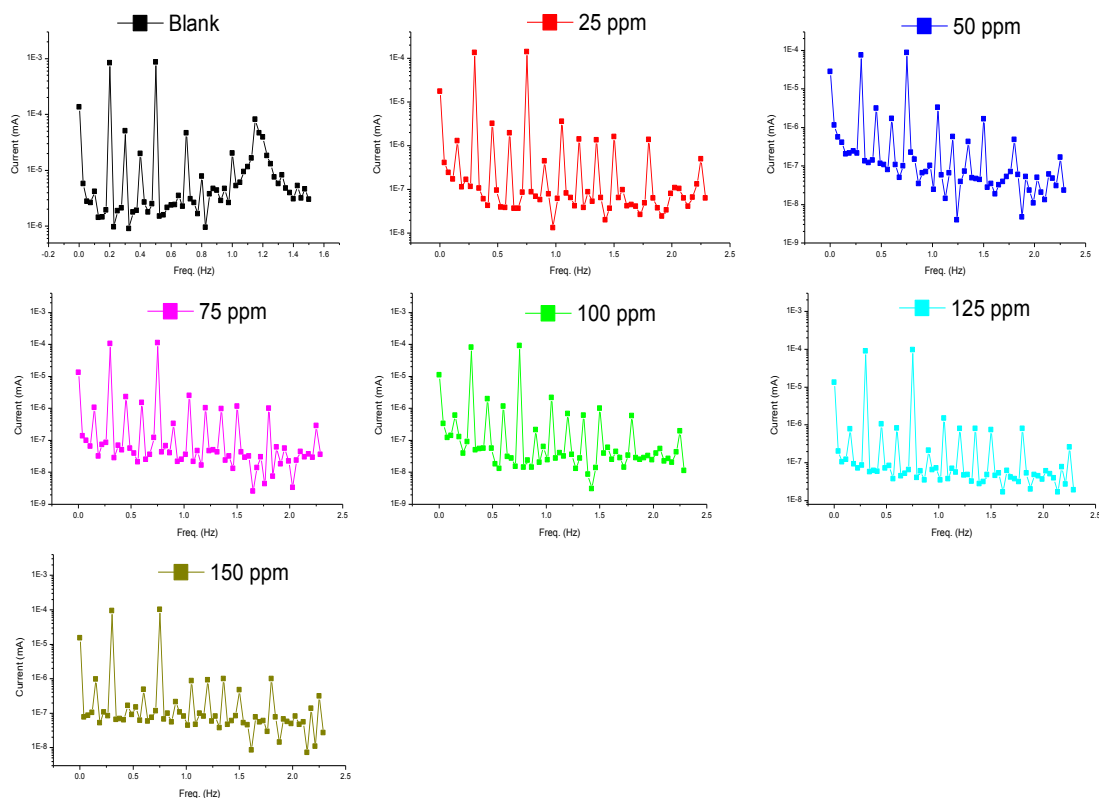
Fig 9. Intermodulation spectrum recorded for CS electrode in 1M HCl solution with and without various doses of Flaxedil at 298 K .

Table 7. The electrochemical kinetic parameters obtained by EFM technique recorded for CS electrode in 1M HCl solutions without and with various dose of Flaxedil at 298K

Conc.,ppm	i_{corr} μAcm^{-2}	β_c $mVdec^{-1}$	β_a $mVdec^{-1}$	CF-2	CF-3	CR mpy	Θ	%IE
0.0	1420	85	116	2.4	3.1	592.1	---	---
25	238	123	109	1.8	2.8	110.7	0.832	83.2
50	205.0	213	134	1.9	3.6	94.5	0.855	85.5
75	193.5	137	114	1.8	3.2	90.0	0.863	86.3
100	155.3	156	129	1.9	3.0	84.6	0.890	89
125	128.6	128	148	1.0	3.6	82.7	0.909	90.9
150	107.1	119	116	1.2	3.1	80.2	0.924	92.4

Quantum chemical calculations: Figure 10 represents the molecular orbital plots and Mulliken charges of investigated inhibitor, Flaxedil; 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 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} is associated of inhibitor, the greater the trend of offering electrons to unoccupied <u>d</u>

729

orbital of the metal, and the higher the corrosion inhibition efficiency, in addition, the lower E_{LUMO}, the easier the acceptance of electrons from metal surface [41].
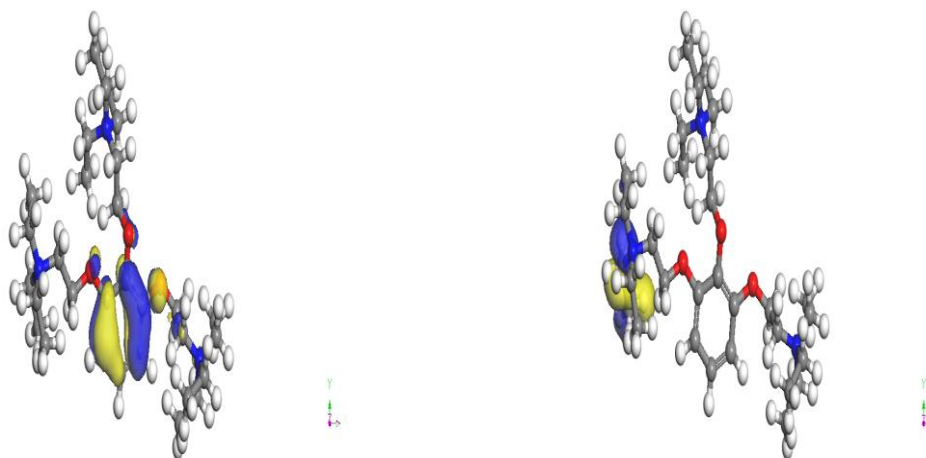
HOMO   LUMO

Fig 10. Molecular orbital plots of inhibitor, Flaxedil

Table 8. Calculated quantum chemical properties for inhibitor, Flaxedil

$-E_{HOMO}$ (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)
14.204	10.37	3.834	1.917	0.522	-12.287	12.287	13.512

From Table 8 it is clear that the low value of ΔE obtained by the four methods in case of inhibitor, Flaxedil, enhance the assumption that Flaxedil molecule 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 there after presents the maximum of inhibition efficiency. 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 [42]. It can be seen that all calculated quantum chemical parameters validate these experimental results.

Scanning Electron Microscopy (SEM) Studies: Figure 11A-C 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 inhibitor, Flaxedil, It is clear that CS surfaces after exposure to 1M HCl solution in absence of inhibitor, Flaxedil, suffer from severe corrosion attack as shown in Figure 11B. On the other hand, the morphology of CS surface is quite different from the previous one when the inhibitor, Flaxedil, is in the solution as shown in Figure 11C where almost not affected by acid corrosion.
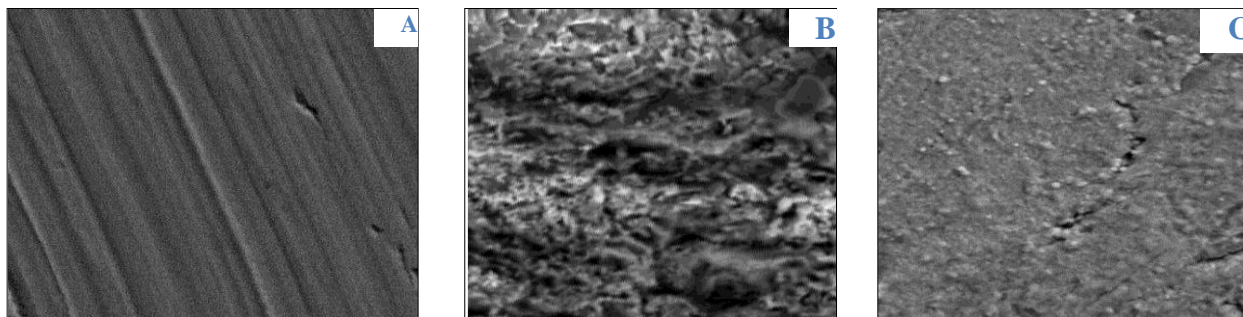
Figure11. SEM micrographs of **A**: CS pure; **B**: CS dipped in 1M HCl solution in absence of drug; **C**: CS dipped in 1M HCl solution after 24 h immersion in in 1M HCl with 150 ppm inhibitor, Flaxedil, all at 298K.

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 Flaxedil on the CS that blocks the active sites present on the CS surfaces. Also may be due to the involvement of inhibitor molecules in the interaction with the reaction sites of CS surface, lead to a decrease in the contact between CS and the aggressive medium, and hence exhibited excellent inhibition effect [43]. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatom with lone pair electrons. However, the compound reported existing in cationic form this form could be attached to the CS surface by means of electrostatic interaction between Cl⁻ and cationic form of Flaxedil since the mild steel surface has positive charge in the acidic medium [44]. This could further be explained based on the assumption that in the presence of Cl^-, the negatively charged Cl^- would attach to positively charged surface and thereby cationic form of Flaxedil being adsorbed to the metal surface. Apart from electrostatic interaction, some chemical interaction is also involved. The non-bonding electrons of hetero atoms and π-electrons of aromatic ring caused chemical interaction.

APPLICATIONS

This study indicates that Flaxedil is a good inhibitor and inhibits CS corrosion by adsorption on its surface.

CONCLUSIONS

The tested inhibitor, Flaxedil, establish a very good inhibition for CS corrosion in HCl solution, where IE% increased by increasing in Flaxedil dose. The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed Flaxedil molecules takes place. Flaxedil inhibits CS corrosion by adsorption on its surface and follows Temkin adsorption isotherm. Polarization curves showed that Flaxedil behaved as mixed-type inhibitor. Double layer capacitances (C_{dl}) decreases with increasing the inhibitor dose, while the charge-transfer resistance (R_{ct}) increases the values of inhibition efficiencies obtained from the different techniques used are compatible with each other.

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