

Journal of Applicable Chemistry

2017, 6 (5): 701-718 (International Peer Reviewed Journal)



Corrosion Protection of Carbon Steel by using Simvastatin Drug in HCl Medium

A. S Fouda^{1*}, G. El-Ewady¹ and Adel H. Ali^{1,2}

Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, EGYPT
 Department of medicinal laboratory, Faculty of medical Science, University of Taiz, YEMEN

Email: asfouda@hotmail.com

Accepted on 10th August 2017, Published online on 27th September 2017

ABSTRACT

Simvastatin drug was utilized as an inhibitor for carbon steel (CS) corrosion in 1 M HCl by utilizing many techniques: weight loss (WL), hydrogen evaluation (HE), open circuit potential (E_{ocp}), electrochemical frequency modulation (EFM), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP) techniques. WL is investigated at various temperatures between (25–45°C) but hydrogen evaluation and all electrochemical studies at room temperature. The inhibition efficiency (% IE), increases with expanding doses of the Simvastatin drug. The activation and the variables of adsorption were investigated and calculated by the effect of temperature on the inhibition of corrosion. The adsorption of the Simvastatin on CS surface was found to obey with Langmuir adsorption model. The morphology of inhibited CS was analyzed by the energy dispersive X-ray spectroscope (EDX), atomic force microscopy (AFM) and scanning electron microscope (SEM). All techniques were utilized to examine the corrosion inhibition of the drug. Polarization data revealed that this drug affect both anodic and cathodic reactions.

Keywords: Corrosion inhibition, HCl, CS, Adsorption, SEM, EDX, AFM.

INTRODUCTION

The most methods for protection of metals from corrosion are investigated by utilization of inhibitors that especially in acid medium [1-2]. The well-known acidic inhibitors are drugs and organic compounds that contain O, S, N (N-heterocyclic), long carbon chain and aromatic compounds. The organic inhibitors have many advantages such as high %IE, cheap, friendly to the environment and easily to produce [3-5]. Pharmaceutical drugs like heterocyclic compounds are used for to reduced corrosion process of Fe, Cu and AI [6-16] in various aqueous medium. Adsorption of the drug facilitate the protection of the metal surface [17]. A few medications such as tetracycline, cloxcillin, azithromycin, ampiclox, ampicillin and orphenadrine were discovered to have a great inhibitors that can compete favorably with green inhibition of corrosion and that most medications can be synthesized from natural products. Selection of some medication as corrosion inhibitors due to the followings: (1) drug molecules contain oxygen, sulphur and nitrogen as active sites, (2) it is environmentally friendly furthermore vital in organic responses and (3) drugs can be easily produced and purified [18-22]. A few medications have been discovered to be a

great corrosion inhibitors for metals such as: Biopolymer gave 86% IE for Cu in NaCl [23], pyromellitic diimide linked to oxadiazole cycle gave 84.6% IE for CS in HCl [24], 2-mercaptobenzimidazole gave 82% IE for CS in HCl [25], Antidiabetic Drug Janumet gave 88.7% IE for MS in HCl [26], Januvia gave 79.5% IE for Zn in HCl[27], Cefuroxime Axetil gave 89.9% IE for Al in HCl [28], Phenytoin sodium gave 79% for CS in HCl [29], Aspirin gave71% IE for MS in H2SO4 [30], Septazole gave 84.8% IE for Cu in HCl [31] and Chloroquine diphosphate gave 80% IE for MS in HCl [32].

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

MATERIALS AND METHODS

Metal sample: The composition of metal sample is listed in (Table 1).

Table 1. The component of the CS under study (wt %)						
Constituent	С	Mn	Р	Si	Iron	
Composition %	0.2	0.6	0.04	0.003	Rest	

Inhibitor: Simvastatin drug is an organic compound which describing in (Table 2). The pharmaceutical drug which was investigated is purchased from Sandozinc and Pfizer inc., companies

Inhibit or	Structur	e	IUPAC Name	Molecular weight	Active center	Chemic al formul a
Simvastatin	HO HO O H O H O O O O O O O O O O O O O		$3R, 7S, 8S, 8aR) - 8 - \{2 -[(2R, 4R) - 4 - hydroxyl -6 - oxotetrahydro - 2H - pyran - 2 - yl]ethyl\} - 3, 7 - dimethyl - 1, 2, 3, 7, 8, 8a - hexahydronaphthalen - 1-yl 2,2-dimethylbutanoate$	418.566 g/mol	5Ο 2π bond	C ₂₅ H ₃₈ O 5

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

Corrosive medium: The corrosive medium is 1M HCl, which prepared by diluted the (%37) HCl with distill water and the different concentrations of inhibitor (50, 100, 150, 200, 250 and 300 ppm) were prepared by dilution

Weight loss (WL) technique: For WL estimations, coins have the area surface (2 cm x 2 cm) x 2 which presented to the destructive solution that utilized. The coins were scraped with SiC polisher sheet coarseness sizes (400, 800 and 1200) and clean with (CH₃)₂CO. At that point clean a few times with bidistilled water, lastly dried by soft tissue. The WL estimations were done in a 100 mL glass measuring beaker put in an indoor regulator thermostat or water path. The coins were then quickly dipped in the test medium in nonexistence and existence dissimilar doses of the examined compound.

All aggressive corrosive medium were opened to air. After three hour, the coins were taken out, washed, dried, and weighted correctly per thirty minutes. The average WL for seven square CS specimens will be obtained.

The % IE and surface coverage (θ) of Simvastatin for the corrosion of CS were determinate from the following equation [33]:

$$IE\% = \theta x 100 = [1 - (W/Wo)] X 100$$
(1)

Where, W^o and W are the WLs in the nonexistence and existence of adding various doses of investigate drug respectively.

Hydrogen evolution (HE) technique: Measurements of HE were estimated at 25°C, and the H₂ volume developed and recorded every 15 minutes, θ and % IE were determination by (3) and (4).

V = K t(2) Where, V is the volume of H₂ in ml, K is rate constant and t is time in minute. $\Theta = 1 - K/K^{\circ}$ (3)

Where, K^{o} and K are the rate constant of corrosion in absence and presence inhibitor, that calculated by plotting V vs. t and K value is the slope.

$$\%$$
 IE = Θ x 100

PP technique: Polarization tests were done in a traditional three-anode cell with a Pt counter electrode terminal and an immersed calomel pool (SCE) as the reference pool. The working electrode which consists of a square sheet from CS settled in epoxy resin like polytetrafluoroethylene which don't affect by acid and covered the coin sample until the level surface that have 1.0 cm² area. The working terminal was polished with SiC polisher papers. Before estimation, the electrode was submerged in corrosive medium at normal potential for 30 min. until the point when an enduring or steady state was come to. The potential of open circuit (E_{ocp}) started in the blank -533 mV and the presence different doses of simvastatin drug started from -497 to 470.2 mV. All tests were done in newly arranged or preparing corrosive medium at room temperature and the data were constantly rehashed no less than three times to check the accuracy or valid results. Determination of % IE and the θ as below [34]:

$$\% IE = \theta \times 100 = \left[1 - \frac{i_{corr(inh)}}{i_{corr(free)}}\right] \times 100$$
(5)

Where, $i_{corr(free)}$ and $i_{corr(inh)}$ are the densities of oxidation current in the nonexistence and existence of Simvastatin drug as an inhibitor, in that order.

EIS technique: All EIS measuring data were performing at open circuit potential E_{ocp} at $25\pm1^{\circ}C$ more than a broad frequency range of $(1\times10^5 \text{ Hz to } \times 0.1 \text{ Hz})$. The perturbation potential was 10 mV in abundance peak to peak. The obtain diameters of the capacitive loops raise in occurrence of Simvastatin drug and indicated of the capacity of the extent of inhibition of oxidation progression, contrary to the diminished of the capacitance of double layers (C_{dl}) which is determination by:

$$C_{dl} = \frac{1}{(2\pi f_{max}R_p)} \tag{6}$$

Where, f_{max} is the highest frequency.

The % IE and the (θ) acquired from the impedance estimations were characterized by the accompanying connection:

$$\% IE = \theta \times 100 = \left[1 - \frac{R_p^o}{R_p}\right] \times 100$$
 (7)

Where, R_p° and R_p are resistance of the charge move in the nonattendance and nearness of Simvastatin, separately.

EFM technique: The large peaks were utilized for the determination of the corrosion current density (i_{corr}), the Tafel inclines (β_c and β_a) and the causality factors CF₂ and CF₃ [35-36]. The % IE_{EFM} was calculated as follows:

$$\% IE_{EFM} = \left[1 - \frac{i_{corr}}{i_{corr}^{o}} \right] \times 100$$
 (8)

www.joac.info

(4)

Where, i_{corr}^{o} and i_{corr} are densities of the corrosion current in the nonexistence and existence of Simvastatin drug. All potentiodynamic, open circuit potential, EIS and EFM as electrochemical analysis were investigated by utilizing Gamry tool PCI300/4.

Surface Examinations: The CS specimens utilized for analysis of surface morphology were prepared in 1M HCl acid (blank) and with 300 ppm of Simvastatin at room temperature for one day after abraded automatically utilizing various emery sheets up to 1200 gravel size. Then, after this the coins were dipped in corrosive medium at even time, the coins were cleaned quietly with distill water, charily dried and mount into the performed specimens examined by using SEM, EDX and AFM.

RESULTS AND DISCUSSION

WL measurement: The WL of CS relative to the surface area at different time periods in the nonexistence and existence of various doses (50, 100, 150, 200, 250 and 300 ppm) of the Simvastatin. The bends lines or curves acquired within the sight of various doses of drug fall essentially underneath that of free corrosive medium as appeared in (Figure-1).

The % IE is recorded in (Table 3). In all cases, the IE of the drug increment with expanding doses of drug but the rate of corrosion was decreased. These results indicated that, the Simvastatin under study is good substance that prevent CS oxidation in corrosive medium.



Figure 1: W L-time bending curves for the oxidation of CS in the nonexistence and existence of various doses of Simvastatin at 25°C

Table 3. Variation of % IE of Simvastatin with various doses at 25°C from WL testing at 120 mindipping in 1 M hydrochloric acid

	11 0	5	
Compound	Conc. ppm	$\frac{k_{corr.} x 10^{-3}}{mg cm^{-2} min^{-1}}$	% IE
Blank		16.25	
	50	5.42	66.7
E.	100	5.00	69.2
istat	150	4.58	71.8
imva	200	4.25	73.9
Š	250	4.00	75.4
	300	3.83	76.4

Temperature effect: Study the effect of temperature by applied Arrhenius equation and the rate of corrosion (k_{corr}) can be determined:

$$\log k_{corr} = A - \left[\frac{E_a}{2.303 RT}\right]$$
(9)

Where, E_a is the activation of inhibition for the oxidation of CS in corrosive medium in nonexistence and existence of Simvastatin inhibitor, R is universal gases constant, T is absolute temperature and A is Arrhenius pre-exponential consistent relies upon the metal sort and electrolyte. Arrhenius plots of log k_{corr} . vs (1/T) for CS in 1 M hydrochloric acid in the nonexistence and existence of various doses of Simvastatin drug is shown graphically in (Figure 2). The variety of log k_{corr} vs (1/T) is straight lines and the estimation of E_a got is recorded in (Table 4). These outcomes propose that the drug is comparative in the system of activity. The expansion in E_a^* with the expansion of various doses of inhibitor, demonstrating that, the energy limit for the oxidation reduction expanded. After additionally shown that the entire procedure is controlled by the relative of surface corroded occurs, since the actuation energy of the consumption oxidation process is > 20 kJ mol⁻¹ [37].

The (ΔS^* , ΔH^*) of activation are determinate from the theory of transition state by applied the following relation [38].

$$k_{corr} = \left[\frac{RT}{Nh}\right] \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right)$$
(10)

Where, N is Avogadro's number, h is Planck's constant. A plot of log (k_{corr}/T) versus (1/T) likewise gave straight lines as appeared in (Figure-3), for CS dissolution in one molar hydrochloric acid in the absence and presence of changed doses of Simvastatin. The slopes of these lines equal $-\Delta H^*/2.303R$ and the intercept rise to log [RT/Nh] + ($\Delta S^*/2.303R$), that the estimation of ΔH^* and ΔS^* were determination and recorded in (Table 4). These outcomes demonstrate that they the used compound acts as inhibitor. The estimations of ΔH^* are reflected the strength of the adsorption of this drug on CS surface. The estimations of ΔS^* without and with the used compound is large and negative; this demonstrates that the rate-deciding step is association rather than dissolution [39].



Figure 2: Diagram (log k_{corr} vs 1/T) for oxidation of CS in HCl acid in the nonexistence and existence of various doses of Simvastatin



Figure 3: Diagram (log k_{corr} / T) vs (1/T) for oxidation of CS in 1 M HCl in the nonexistence and existence of variant doses of Simvastatin at 25°C.

Table 4. E_a^* , ΔH^* and ΔS^* variables for the oxidation of CS in 1 M hydrochloric acid in the nonexistence and existence of variant doses of tested drug

Conc.			
Pnm	E [*] a kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹
Blank	42.3	40.4	142.2
50	53.8	52.1	111.5
100	54.1	52.5	111.4
150	54.9	53.4	109.9
200	57.5	55.9	102.5
250	62.1	60.9	87.9
300	67.0	65.9	72.8

Adsorption isotherms: Simvastatin adsorbed on the metal and the values of (θ) for various doses of drug in one molar hydrochloric acid was determinate from WL data utilizing the follows relation:

$$\boldsymbol{\theta} = \left[\frac{weight \, loss_{(pure)} - weight \, loss_{(inh)}}{weight \, loss_{(pure)}}\right]$$
(11)

From the Θ values, it is obvious that increment with raising the doses of Simvastatin. By utilizing these values and for applying various adsorption isotherms Langmuir adsorption was found the best one and to follow the next relation [40].

$$C/\theta = 1/K_{ads} + C$$

(12)

Where, $K_{ads.}$ is the equilibrium constant of adsorption. Plotting (C/ Θ) against (C) of Simvastatin at various temperatures is shown in (Figure-4). The linear relationship is given with intercept equal to (1/K_{asd.}) and slope similar the unity, the adsorption constant being result to the standard free energy of ΔG°_{ads} by follows:

$$\Delta G_{ads}^{o} = -RT ln \left(55.5 K_{ads} \right) \tag{13}$$

Where, R is the gerenral gas constant, T is the absolute temperature and 55.5 is the doses of water in the solution in M/L. The $\Delta G^{o}_{ads.}$ values at all studied at different temperatures which determined by above equation (13) and recorded in (Table 5). The ($\Delta H^{o}_{ads.}$) was determined according to the Van't Hoff equation [41].

$$\log k_{ads} = \left(\frac{-\Delta H_{ads}}{2.303RT}\right) + constant$$
(14)

Plotting (log K_{ads.}) against (1/T) give straight lines as shown in (Figure-5), the straight lines give slope equal ($\Delta H^{o}_{ads.}/2.303R$), from this slope; the ΔH^{o}_{ads} values were calculated and are listed in (Table 5). Then by applying the following equation:

 $\Delta G^{o}_{ads} = \Delta H^{o}_{ads.} - T\Delta S^{o}_{ads.}$

(15)

From introducing the values of ΔG^{o}_{ads} and $\Delta H^{o}_{ads.}$, the ΔS^{o}_{ads} was calculated at all studied temperatures from the above eq. (15). All thermodynamic adsorption parameters for Simvastatin inhibitor on CS from 1M HCl medium can be concluded that:

- 1- The correlation coefficients between (0.99 0.98) reflected that the experimental data give good curves fitting for the adsorption isotherm, and K_{ads} values increase with increasing temperatures from 25 to $45^{\circ}C$
- 2- The negative values of ΔG^{o}_{ads} reflect that the adsorption of Simvastatin on CS surface in 1 M hydrochloric acid solution is spontaneous process.
- 3- The ΔG^{o}_{ads} values are around -20 kJ mol⁻¹ or less lead to the Van Der Waal's forces or electrostatic attraction between positive charged of metal surface or vacant space in valance orbital's of the metal surface accepted electrons to form semi coordination bond and the negative charge of Simvastatin molecules in the bulk of the medium i.e. physical adsorption.
- 4- The negative sign of ΔH^{o}_{ads} refer to the adsorption of inhibitor molecules is an exothermic process, indicating that the adsorption is physical adsorption. The unshared pairs electron from investigate molecule may attractive with positive center on the surface of CS by electrostatic attraction to provide a protective film prevent corrosion process [42].
- 5- The ΔS^{o}_{ads} values, in the existence of the investigate drug are negative and large that is accompanied with exothermic adsorption process [43].



Figure 4: Diagram illustrate the Langmuir adsorption that plotted (log C) against (C/θ) of the simvastatin drug for corrosion of CS in 1 M HCl from WL technique at 25°C

Table 5.	K_{ads} and adsorption free energy (ΔG°_{ads}) for the adsorption of Simvastatin on CS	in 1 M
	hydrochloric acid from WL method at 25°C	

Temp. °C c	$egin{array}{c} K_{ads} \ M^{-1} \end{array}$	-ΔG° _{ads} kJ mol ⁻¹	-ΔH ^o _{ads} kJ mol ⁻¹	$-\Delta S^{o}_{ads}$ J mol ⁻¹ K ⁻¹
25	42.55	19.25		3.06
30	28.44	18.55		5.30
35	26.79	18.71	20.16	4.72
40	24.17	18.74		4.52
45	24.63	19.09		3.36

HE tests: All information drowns from the volume of hydrogen which produces versus time, from the different doses (50 - 300 ppm) of Simvastatin that shown in (Figure-6). The slope of lines evaluated of the rate of corrosion. The great straight lines are shown that the insoluble film on the metal surface. The certain of the rate of corrosion acquired from hydrogen evaluation individually at various doses are recorded in (Table 6). The rate of corrosion reduced with increasing of Simvastatin doses.



Figure 5: (log K_{ads}) vs (1/T) for the corrosion of CS in 1M HCl in the existence of Simvastatin at various temperatures

Table 6. The rate of corrosion for metal at presence different doses of Simvastatin inhibitor

Conc.	k _{corr}		
		Θ	% IE
ppm	ml cm ⁻² min ⁻¹		
Blank	0.158		
50	0.062	0.608	60.8
100	0.059	0.627	62.7
150	0.056	0.646	64.6
200	0.053	0.665	66.5
250	0.050	0.684	68.4
300	0.046	0.709	70.9



Figure 6: HE produced versus time with and without various doses of drug at 25°C

Open circuit potential (E_{ocp}): From the (Figure-7) is shown several interesting points:

1. The E_{OPC} in the blank solution is beginning from -533 mV then shifted anodically and reached the steady state after 300 second indicating that the initial dissolution process and formation oxide film on the metal surface.

2. The E_{OCP} is started in the existence of Simvastatin, at less negatively potential compared with that in the nonexistence of the drug and then shifted anodically, according to the increasing the doses 50, 100, 150, 200, 250 and 300 respectively, that shown in (Table 7). The steady state is attained rapidly, with increasing the doses of the drug comparing with the blank, and then the shift in the potential of E_{OCP} increment in the positive direction position and the drug might certain act as an anodic inhibitor [44]. However, from (Figure-7), the shift in E_{OCP} on addition Simvastatin is about 57.5 mV revealing that the present drug acts as anodically drug.



Figure 7: Open circuit potential, E_{ocp} vs. time relations for CS submersion in 1M hydrochloric acid in the nonexistence and existence of Simvastatin drug at 25°C

Conc. Ppm Simvastatin	-E _{Min} (mV)	-E _{Max} (mV)
Blank	533.0	502.0
50	497.5	399.2
100	488.2	466.5
150	481.6	442.5
200	476.6	454.4
250	473.3	457.1
300	470.2	432.6

Table 7. E_{ocp} of the CS in the nonexistence and in existence of Simvastatin drug at 25°C

PP tests: PP is carrying out in 1 M HCl acid medium in the nonexistence and existence of different doses of Simvastatin at 25° C. The results are drowning in (Figure-8). The PP variables are recorded in (Table 8). These outcomes information showing that the cathodic and anodic bends lines gotten by Tafel-type behavior. The type of the bends lines is fundamentally the same which shows the dissolution of the mechanism of CS and hydrogen evolution obviously stay without changing. Expansion of Simvastatin reduces the corrosion current. The small change of the E_{corr} revealed that the drug acts as mixed one [45].

The information data additionally demonstrate that the inclines of the anodic and the cathodic Tafel slants ($\beta_a \& \beta_c$) were slightly changed on expanding the doses of the used compound. This demonstrates that there is no change of mechanism but % IE increment with expanding doses of simvastatin.

The way of the approximations of β_c are somewhat higher than the approximations of β_a this is attributed to the cathodic activity of the drug. The steadiness and the cathodic incline gotten from the electrochemical estimations demonstrate that the hydrogen evolution reaction was activation controlled [46] when the adding of the Simvastatin did not alter the mechanism of this process.



Figure 8: The PP curves for the oxidation of CS in 1M HCl in the nonexistence and existence of varied doses of Simvastatin at 25°C

 $\label{eq:corr} \mbox{Table 8. The effect of doses of Simvastatin on the E_{corr}, i_{corr}, $Tafel slopes ($\beta_a \& β_c)$, $\%$ IE , and Θ for the oxidation of CS in 1M HCl at 25 °C $$$

Conc.	I _{corr.}	-E _{corr.}	β_a	β _c	C. R.	θ	% IE
ppm	mA/cm ⁻²	mV(SCE)	mV dec ⁻¹	mV dec ⁻¹	Мру	Ű	/0 IL
0.0	147	480	166	208	67.3		
50	63.8	476	118	118	29.14	0.578	57.8
100	63.4	468	79.9	129	28.97	0.580	58.0
150	59.4	476	112	109	27.14	0.607	60.7
200	58.2	462	63.3	114	26.58	0.615	61.5
250	42.6	482	88.5	94.9	19.45	0.718	71.8
300	30.5	464	40.1	70.9	13.96	0.798	79.8

EIS tests: The (EIS) charts (Nyquist and bode) at frequencies extending range between 0.1 Hz to 10^5 Hz with 10 mV plenitude position at OCP for CS in one molar hydrochloric acid in the nonexistence and existence of varied measurements of Simvastatin doses are acquired. The identical circuit that describe for (CS) and electrolyte are found in (Figure-9), EIS variables and % IE were determined and recorded in (Table 9). The obtained Nyquist and Bode that are plotting in curves for Simvastatin are shown in (Figure-10). Nyquist spectra are described by a semicircle. These demonstrate that the oxidation of CS is restricted by a charge transfer process [47]. The diameter of the capacitive circle acquired increments within the sight of Simvastatin were demonstrated that the expanding the level of inhibition of the consumption oxidation process [48].

From the results of (EIS) that obtained R_p rises and C_{dl} reducing with increasing of Simvastatin drug doses. The increase in R_p values improve the increase of the % IE because of the progressive substituent of water particles by the adsorption of the medication particles on the metal surface by an adherence film form on

the metal surface. The formation film on the metal surface reduced the double layer thickness. Also, the decreasing of C_{dl} with rises the drug doses as result from reduce in local dielectric constant which indicating that, the drug was adsorbed on anodic sites and covered the cathodic sites on the surface of the metal [49].



Figure 9: Circuit model used to fit the experimental data, R_s refer to solution resistance and R_p or R_{ct} charge transfer resistance, respectively



Figure 10: The Nyquist (a) and Bode (b) plots for oxidation of CS in one 1M HCl in the nonexistence and existence of various doses of Simvastatin at 25 °C

Conc.	R _p	C _{dl}	θ	% IF
ppm	$\Omega \text{ cm}^2$	$\mu F cm^2$	0	70 IL
0.0	64.7	594		
50	170.6	69	0.621	62.1
100	205.5	55.9	0.685	68.5
150	225.5	49.3	0.713	71.3
200	258.1	36.9	0.749	74.9
250	278.7	29.9	0.768	76.8
300	280.9	27.4	0.769	76.9

 Table 9. Electrochemical kinetic variables occur by EIS technique for oxidation of CS in 1M HCl

 nonexistence and existence various doses of Simvastatin at 25 °C

EFM tests: EFM is regarded a very good technique to determination corrosion information directly and quickly because EFM is nondestructive technique to determination corrosion [50]. The measurements data of EFM are become a valid data when the practical causality factors (CF2 and CF3) are equals or near the hypothetical values (2 and 3) which determination from the frequency spectrum of the current reaction. (Figure-11), illustrated the EFM inter-modulation spectrum of CS in 1 M hydrochloric acid in nonexistence and existence deferent doses of Simvastatin drug. It clearly that the treatment EFM data utilizing two various models: (1) the activation model by solved three nonlinear equation and assuming no change of the corrosion potential due to the polarization of the working electrode (2) cathodic reaction controlled by complete diffusion [51].

The density of corrosion current (i_{corr}), the (β_a and β_c) and (CF2 and CF3) are calculated from the two large peaks of inter-modulation spectrum, and then recorded in (Table 10). It is obviously, that the addition of tested Simvastatin at given doses to the corrosive medium reducing the (i_{corr}), indicating that the Simvastatin inhibits the corrosion of CS by the adsorption process. The (CF2 and CF3) are equal to the hypothetical values (2 and 3) indicative of that the estimation information are valid and good value [52]. The % IE _{EFM} values are increments by expanding the doses of Simvastatin which determination and recorded in (Table 10).



Figure 11: EFM for CS in 1M HCl with and without various doses of the used Simvastatin

Comp.	Conc. M	i _{corr.} µAcm ⁻²	$\beta_a \ge 10^{-3}$ mVdec ⁻¹	$\beta_c \ge 10^{-3}$ mVdec ⁻¹	CF (2)	CF (3)	CR Mpy	Θ	%IE
Blank	0.0	350.3	156.4	247.9	1.5	2.9	160.1		
	50	100.9	92.3	99.4	1.6	3.5	46.1	0.712	71.2
tin	100	98.3	104.7	119.0	1.2	3	44.9	0.719	71.9
ısta	150	96.5	98.3	107.1	1.9	5.4	44.1	0.724	72.4
nva	200	94.2	104.6	115.8	2	3.3	43.0	0.731	73.1
Sir	250	92.7	132.7	183.3	2	5	42.4	0.735	73.5
	300	89.2	81.0	111.3	1.8	4	40.8	0.745	74.5

Table 10. Electrochemical kinetic variables occur by EFM method for CS in 1 M HCl nonexistence andexistence different doses of Simvastatin at 25 °C

SEM analysis: (Figure-12), refer the micro-graph obtain for CS coins in existence and in nonexistence of 300 ppm of Simvastatin after contact for 1 day submersion. It is obvious that CS surfaces help and enhance corrosion aggression in corrosive medium by inter-granule corrosion. The coin morphology of CS surface is smooth before immersion in the corrosive medium with 300 ppm of Simvastatin drug which adsorbed on surface of metal and formation thin film. We are clear that the development of a film which is dispersed in a request route in general or in the whole surface of the CS. This might be because of the adsorption of the Simvastatin on the CS surface and make the passive film keeping in mind the end goal to obstruct the dynamic site introduce on the CS surface. The inhibitor particle association with dynamic locales of CS surface, resulting in a reduction in the contact between CS and the destructive medium and consecutively displayed superb restraint impact [53-54]



Figure 12: SEM micrographs for CS in the nonexistence and existence of 300 ppm of Simvastatin for 1 day

EDX analysis: To determination of existence elements which adsorbed on CS surface by EDX spectrum after I day immersion in one molar hydrochloric acid with optimum doses of Simvastatin drug. (Figure-13), gives the EDX examination of CS in one molar hydrochloric acid with within the sight of 300ppm of Simvastatin. The spectrum demonstrates extra lines, showing the presence of C (inferable from the carbon atoms of some Simvastatin). This information demonstrates that the C and O atoms secured the coins surface. The elements carbon and oxygen was determination by EDX analysis and shown that passivation film contained the chemical formula of Simvastatin drug adsorbed on the surface of CS. It is seen that, the percent weight of adsorb elements C and O were present in the spectra and recorded in (Table 11).



Figure 13: EDX examination on CS in the existence and nonexistence of Simvastatin for 1 day submersion.

 Table 11. Surface composition (% wt) of CS after one day of submersion in 1M HCl nonexistence and existence the 300 ppm of Simvastatin

(Mass %)	Fe	С	0	Ν	S	Cl
Pure metal	98.28	0.78				
Blank	72.1	9.23	17			0.35
Simvastatin	62.16	1.32	33.54	1.14		1.63

AFM analysis: From the analysis, it can be gained regarding the roughness on the surface. The roughness profile values play an important role in identifying and report the efficiency of the inhibitor under study. Among the roughness take a role in explanation about the nature of the adsorbed film on the surface [55-56]. (Figure-14), shows the 3D images as well as elevation profiles of polished of CS in absence and existence Simvastatin as an inhibitor. It observed in (Figure-14), the surface of CS specimen (a) exposed to corroded solution affected vales structure with large and deep crack but the surface (b) reveal that is covering film adsorbed on the metal surface. The conclusion, that the adsorption film can protect the surface of the metal from corrosion process. Analysis of the values indicated higher the values of roughness parameter reached. The mean roughness is found to be $(2.60 \ \mu\text{m})$ for the blank in acid solution which placed in 1M HCl one day and analyzed. The observation of the metal surface which submersion in 1M HCl in existence of 300 ppm of Simvastatin inhibitor possesses roughness (711.74 nm) compared to the blank solution. It can be noted that the value is less than that of the blank value. The diminishing in the roughness value reflected the adsorption of Simvastatin drug molecule on metal surface thereby reducing the rate of oxidation.



(b)

Figure 14: The 3D of optical images of AFM in nonexistence (a) and existence (b) of Simvastatin drug

CONCLUSIONS

The inhibition of the consumption oxidation of CS in 1M HCl as a corrosive medium by Simvastatin is dictated by WL, hydrogen evaluation, potentiodynamic estimations, EIS, EFM, SEM, EDX and AFM examination.

- 1) The tried Simvastatin inhibitor set up a decent restraint for CS corrosion in HCl as the corrosive medium
- 2) Simvastatin inhibit the CS by adsorption on its surface and make thin film layer adsorbed on the surface of metal.
- 3) The %IE of the inhibitor increments with expanding of their doses.
- 4) Capacitances of double layer are diminishing with respect the blank corrosive medium when the Simvastatin included. This reality may clarified by adsorption of the Simvastatin particle on the CS surface.

- 5) Adsorption of Simvastatin compound on CS surface in HCl solution applicable by Langmuir adsorption model.
- 6) The estimations of % IE acquired from the diverse free procedures utilized demonstrated the valid of the occur results.

REFERENCES

- [1] G. Trabanelli, inhibitors an old remedy for a new challenge, *Corrosion*, **1991**, 47, 410-419.
- [2] D.N.Singh and A.K. Dey, Synergistic Effects of Inorganic and Organic Cations on Inhibitive Performance of Propargyl Alcohol on Steel Dissolution in Boiling Hydrochloric Acid Solution, *Corrosion*, **1993**, 49, 594-600.
- [3] G. Banerjee and S.N. Malhotra, Contribution to the adsorption of aromatic amines on mild steel surfaces from HCl solutions by impedance, UV and Raman spectroscopy, *Corrosion-NACE*, **1992**, 48, 10-15.
- [4] S.T. Arab and E.A. Noor, Inhibition of Acid Corrosion of Steel by Some S-Alkylisothiouronium Iodides, *Corrosion*, **1993**, 49,122-129.
- [5] I. A. Raspini, Influence of Sodium Salts of Organic Acids as Additives on Localized Corrosion of Aluminum and Its Alloys, *Corrosion*, **1993**, 49, 821-828.
- [6] N. Hajjaji; I. Ricco, A. Srhiri, A. Lattes, M. Soufiaoui, A. Benbachir, Effect of N-Alkylbetaines on the Corrosion of Iron in one molar hydrochloric acid Solution, *Corrosion*, **1993**, 49, 326-334.
- [7] M. Elachouri, M.S. Hajji, M. Salem, S. Kertit, R. Coudert, E.M. Essassi, Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution, *Corros.Sci.*, **1995**, 37, 381-389.
- [8] H. Luo, Y.C. Guan, K.N. Han, Inhibition of mild steel corrosion by sodium dodecyl benzene sulfonate ... and Sodium Oleate in Acidic Solutions, *Corrosion*, **1998**, 54, 619-627.
- [9] M.A. Migahed, E M S. Azzam, A.M. Al-Sabagh, Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant, *Mater. Chem. Phys.*, **2004**, 85, 273-279.
- [10] M.M. Osman, A.M.Omar, A.M. Al-Sabagh, Corrosion inhibition of benzyl triethanol ammonium chloride and its ethoxylate on steel in sulphuric acid solution, *Mater. Chem. Phys.*, **1997**, 50, 271-274.
- [11] F. Zucchi, G. Trabanelli, G. Brunoro, The influence of the chromium content on the inhibitive efficiency of some organic compounds, *Corros.Sci.*, **1992**, 33, 1135-1139.
- [12] R.F.V. Villamil, P. Corio, J.C. Rubim, M.L. Siliva Agostinho, Effect of sodium dodecylsulfate on copper corrosion in sulfuric acid media in the absence and presence of benzotriazole, J. *Electroanal.Chem.*, **1999**, 472 ,112-119.
- [13] T.P. Zhao, G.N. Mu, The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, *Corros.Sci.*, **1999**, 41, 1937-1944.
- [14] S.S. Abd El Rehim, H. Hassan, M A. Amin, Corrosion inhibition of aluminum by 1,1(lauryl amido) propyl ammonium chloride in HCl solution, *Mater. Chem. Phys.*, **2001**, 70, 64-72.
- [15] S.S. Abd El Rehim, H. Hassan., M,A. Amin, The corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminium and its alloys in 1.0 M HCl solution, *Mater. Chem. Phys.*, 2003, 78, 337-348.
- [16] R. Guo T. Liu, X. Wei, Effects of SDS and some alcohols on the inhibition efficiency of corrosion for nickel, *Colloids Surf.*, *A*, **2002**, 209, 37-45.
- [17] V. Branzoi, F. Golgovici, F. Branzoi, Aluminium corrosion in hydrochloric acid solutions and the effect of some organic inhibitors, *Mater. Chem. Phys.*, **2002**, 78, 122-131.
- [18] F. Bentiss Traisnel, M. Lagrenee, The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, *Corros.Sci.*, **2000**, 42, 127-146.
- [19] M.A.B. Christopher, A.R.G. Isabel Jenny, The electrochemical behaviour and corrosion of aluminium in chloride media. The effect of inhibitor anions, *Corros.Sci.*, **1994**, 36, 915-923.

- [20] M. Elachouri, M.S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, Some Nonionic Surfactants as Inhibitors of the Corrosion of Iron in Acid Chloride Solutions, *Corrosion*, 1996, 52, 103-108.
- [21] A.S. Algaber, E.M. El-Nemma, M.M. Saleh, Effect of octylphenol polyethylene oxide on the corrosion inhibition of steel in 0.5 M H2SO4, *Mater. Chem. Phys.*, **2004**, 86, 26-32.
- [22] V. Branzoi, F. Golgovici, F. Branzoi, Aluminium corrosion in hydrochloric acid solutions and the effect of some organic drugs, *Mater. Chem. Phys.*, **2002**, 78, 122-131.
- [23] R. Oukhrib, B. El Ibrahimi, H. Bourzi, K. El Mouaden, A. Jmiai, S. El Issami, L. Bammou, L. Bazzi; Quantum chemical calculations and corrosion inhibition efficiency of biopolymer "chitosan" on copper surface in 3%NaCl, *JMES*, 2017, 8 (1): 195-208.
- [24] A. M. Al-Azzawi and K. K. Hammud, Newly antibacterial/anti-rusting oxadiazoleporomellitic diimids of CS / hydrochloric acid interface: Temkin isother model, *IJRPC*, **2016**, 6(3): 391-402.
- [25] L. El Ouasif, I. Merimi, H. Zarrok, M. El ghoul, R. Achour, M. Guenbour, H. Oudda, F. El-Hajjaji and B. Hammouti, Synthesis and inhibition study of CS corrosion in hydrochloric acid of a new surfactant derived from 2-mercaptobenzimidazole, *J. Mater. Environ. Sci*, **2016**, 7 (8): 2718-2730.
- [26] U. M. Sani and U. Usman, Electrochemical Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium Using the Antidiabetic Drug Janumet as Drug, *International Journal of Novel Research in Physics Chemistry & Mathematics*, 2016, 3(3): 30-37.
- [27] A.M. Kolo, U.M. Sani, U. Kutama and U. Usman, *The Pharmaceutical and Chemical Journal*, **2016**, 3(1), 109-119.
- [28] P. O. Ameh and U. M. Sani; Cefuroxime Axetil: A Commercially Available Pro-Drug as Corrosion Drug for Aluminum in Hydrochloric Acid Solution, *Journal of Heterocyclics*, 2015, 1(1), 2-6.
- [29] H. I. Al-Shafey, R. S. Abdel Hameed, F. A. Ali, A. S. Aboul-Magd, M. Salah, Effect of Expired Drugs as Corrosion Drugs for CS in 1M HCL Solution, *Int. J. Pharm. Sci. Rev. Res.*, 2014, 27(1):146-152.
- [30] R. Kushwah and R. K. Pathak; Inhibition of Mild Steel Corrosion in 0.5 M Sulphuric Acid Solution by Aspirin Drug, *International Journal of Emerging Technology and Advanced Engineering*, **2014**, 4(7), 880-884.
- [31] A. S. Fouda, M.N. EL-Haddad and Y.M.Abdallah, Septazole: Antibacterial Drug as a Green Corrosion Drug for Copper in Hydrochloric Acid Solutions, *IJIRSET*, **2013**, 2 (12): 7073-7085.
- [32] S. U. Ofoegbu and P. U. Ofoegbu; Corrosion inhibition of mild steel in 0.1 M hydrochloric acid media by chloroquine diphosphate, *ARPN Journal of Engineering and Applied Sciences*, 2012, 7 (3): 272-276.
- [33] G.N. Mu, T.P. Zhao, M. Liu, T. Gu, Effect of Metallic Cations on Corrosion Inhibition of an Anionic Surfactant for Mild Steel *,Corrosion,* **1996**, 52, 853-856,
- [34] J. Lipkowski, P. N., Ross (Eds.), Adsorption of Molecules at Metal Electrodes, **1992**, VCH, New York.
- [35] S. L. F. A. Da Costa and S. M. L. Agostinho, Electrochemical studies of cu-Al Alloys in Sulphate SciELO, *Corrosion*, **1989**, 45, 472 477.
- [36] J. Aljourani, K. Raeissi, M.A. Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution, *Corros. Sci.*, **2009**, 51, 1836-1843.
- [37] H. Amar, A. Tounsi, A. Makayssi, A. Derja, J. Benzakour, A. Outzourhit, Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media, *Corros.Sci.*, 2007, 49, 2936-2945,.
- [38] M.A. Migahed, E.M.S. Azzam, S.M.I. Morsy, Electrochemical behaviour of CS in acid chloride solution in the presence of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles, *Corros.Sci.*, **2009**, 51, 1636-1644.
- [39] S. Bllglc, N. Caliskan, An investigation of some Schiff bases as corrosion inhibitors for austenitic chromium-nikel steel in H₂SO₄, *Applied Electro-chemistry*, **2001**, 31, 79-83.

- [40] H. Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, Inhibition effect of polyethylene glycol on the corrosion of CS in sulphuric acid, *Mater.Chem.Phys.*, **2005**, 92, 480-486.
- [41] A. El Maghraby, T. Y. Soror, Efficient surfactant as corrosion inhibitor for CS in hydrochloric acid solutions, *Adv. App. Scie.*, **2010**, 1, 156–168.
- [42] I. Al-shafey, M. A. Abass, A. A. Hassan, S. A. Sadeek, Corrosion inhibition of CS in 1M HCl Solution by Schiff base compound obtained from 1,3-Diaminopropane, *IJABC*, 2014, 3, 1004 -1015.
- [43] A. S. Fouda, M. M. Gouda, and S. I. Abd El-Rahman, Benzaldehyde, 2-Hydroxybenzoyl Hydrazone Derivatives as Inhibitors of the corrosion of Aluminium in hydrochloric Acid, *Chem. Pharm. Bull.*, 2000, 48 (5), 636-640.
- [44] O. A. Hazazi, A. Fawzy, M. Awad; Synergistic Effect of Halides on the Corrosion Inhibition of Mild Steel in H2SO4 by a Triazole Derivative: Kinetics and Thermodynamic Studies, Int. J. Electrochem. Sci., 2014, 9, 4086 – 4103.
- [45] A. S. Fouda, A. M. El- Defrawy and M. W. El-Sherbeni, Pharmaceutical compounds as save corrosion inhibitors for CS in 1M H₂SO₄ solution, Reprint form the Mansoura, *J, Chemistry*, **2012**, 39 (2) 1-27.
- [46] A.S. Fouda, A.A. Al-Sarawy, E.E. El-Katori, Pyrazolone derivatives as corrosion inhibitors for Mild steel HCl solution, *Desalination*, **2006**, 201, 1-13.
- [47] A. A. Farag, I. M. Ibrahim, Influence of Nonionic Surfactant on the CS Corrosion in Hydrochloric Acid Solution, *IJSR*, **2014**, 3, 1087-1091.
- [48] O. Benalli, L. Larabi, M. Traisnel, L. Gengembra, Y. Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on mild steelin one molar hydrochloric acidO₄, *Appl. Surf. Sci.*, **2007**, 253, 6130-6139.
- [49] S. Kshama Shetty, A. Nityananda, Shetty, Ionic Liquid as an Effective Corrosion inhibitor on 6061Al-15 Vol.PCT.SIC_(p) Composite in 0.1M H₂SO₄ Medium, An Ecofriendly Approach, 2015, 3, 41-64,.
- [50] E. Kus, F. Mansfeld, an Evalation of the Electrochemical Frequency Modulation (EFM) Technique, *Corros. Sci.*, **2006**, 48, 965-979.
- [51] G. A. Caigman, S. K. Metcalf, E. M. Holt, Thiophene substituted dihydropyridines, *J.Chem. Cryst.*, **2000**, 30, 415-422.
- [52] R.W. J., Bosch Hubrecht, W.F., Bogaerts, B.C., Syrett,: Electrochemical Frequency Modulation: A New Electrochemical Technique for Online Corrosion Monitoring, *Corros. Sci.*, 2001, 57, 60-70.
- [53] A. S. Fouda, Y. M. Abdallah, D. Nabil, Dimethyl pyrimidine Derivative as Corrosion inhibitors for CS in Hydrochloric Acid solutions, *IJIRSET*, **2014**, 3,12965-12982.
- [54] Y. Yelri, Enriadi, N. Jamarun, Gunawarman, Corrosion Inhibition Efficiency of mild Steel in Hydrochloric Acid by Adding theobroma Cacao Feel Extract, *BCES*, **2014**,14, 15-19.
- [55] H. Otmocic Curkovic, K. Marusic, E. Stupnisek-Lisac, and J. Telegdi, Electrchemical and AFM study of Corrosion linhibition with Respect to Application Method, *Chem. Biochem. Eng. Q.*, 2009, 23 (1) 61- 66.
- [56] S. B. Pralhibha, P. Kotteeswaran, V. Bheema Raju, Study on the inhibition of MU steel Corrosion by Cationic Surfactant in HCl Medium, *IOSR Journal of Applied Chemistry (IOSRJAC)*, **2012**, 2, 45-53.

AUTHOR ADDRESS

1. A. S Fouda

Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt E-Mail: asfouda@hotmail.com, Tel: +20502365730

