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RESEARCH ARTICLE

Actonel, Fosamax, Etidron as Save Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solutions

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The inhibiting effect of some pharmaceutical drugs on the corrosion of carbon steel in 0.5M HCl was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrical frequency modulation (EFM) and surface examination using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques. The results of weight loss showed that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature. Potentiodynamic polarization studies have shown that these compounds suppress both the cathodic and anodic processes and thus acted as mixed-type inhibitors. The adsorption of these compounds on carbon steel surface was found to follow the Langmuir isotherm. The effect of temperature on corrosion inhibition has been studied and thermodynamic activation and adsorption parameters were calculated and discussed.

Introduction

Acid solutionsare widely used in industry, with important fields of application including acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. Among acidic media, the hydrochloric acid used in the pickling of metals, the acidification of oil wells and the cleaning of scales is more economical, efficient and straight forward compared to other mineral acids [1].The use of inhibitors is one of the most practical methods for protection against corrosion and prevention of unexpected metal dissolution and acid consumption, especially in acid solutions. Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosive attack. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S,O, P or Na atoms in the molecule heterocyclic Compounds and p-electrons [2]. Such compounds can adsorb onto the metal surface and block the active surface sites, thus reducing the corrosion rate. Although many synthetic compounds show good anticorrosive activity, most of the more highly toxic to both human beings and the environment [3], and they are often expensive and non-biodegradable. Thus, the use of pharmaceutical drugs as corrosion inhibitors has becomea key areaof research. The investigated pharmaceutical drugs offer interesting possibilities for corrosion inhibition and are of particular interest because of their safe use, high solubility in water, with high molecular size and containing electronegative atoms such as nitrogen, phosphorus ,and oxygen in their molecules, such these compounds should be good corrosion inhibitors.

The aim of this study is to investigate the inhibition effect of some pharmaceutical drugs named Actonel, Fosamax & Etidron on the corrosion of carbon steel in 0.5M HClusing weight loss,

potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrical frequency modulation (EFM), and Surface examination using SEM & EDX techniques.

2. Experimental methods

2.1. Materials

The experiments were performed with carbon steel type C1018 with the following composition:

Rectangular specimens with dimensions were used for weight loss measurements. For electrochemical tests, the exposed surface area of carbon steel was 1 cm^2.

2.2. Inhibitors and chemicals.

The pharmaceutical compounds have been investigated named Actonel, Fosamax & Etidron from purchased from Procter & Gamble, Merck sharp& Dohme and Memphis companies respectively. The used pharmaceutical drugs are chosen because: they are easily soluble in water, have high molecular weights, and contain many donating atoms (N, S and P). They arefrom analar grade and used without further purifications. All the solutions were prepared using AR grade chemicals in bidistilled water. The aggressive solutions used were made from 37 % HCl, appropriate concentrations of acid were prepared using bidistilled water. 10^{-3} M stock solutions from the investigated inhibitors were prepared by dissolving the appropriate weights of the solid pharmaceutical drugs in bidistilled water, the other concentrations of pharmaceutical drugs (1 x 10^{-6} – 21 x 10^{-6} M) were prepared by dilution with bidistilled water. All the materials used were of AR grade and used as received.

2.2. Procedures

2.2.1. Weight loss measurements

For weight loss measurements, square specimens of size 2 x 2 x 2cm were used. The specimens were abraded with emery papers grit sizes (400, 800, 1200 and 2000), degreased with acetone. Then rinsed several times with bidistilled water, and finally dried between two filter papers. The weight loss measurements were carried out in a 100 ml capacity glass beaker placed in water thermostat bath. The specimens were then immediately immersed in the test solution without or with desired concentration of the investigated pharmaceutical compounds. Triplicate specimens were exposed for each condition and the mean weight losses were reported.

The % inhibition efficiency (% IE) and degree of metal surface coverage (θ) have been calculated using the relations:

$$\% IE = \theta \times 100 = [1- (\Delta W_{inh}/\Delta W_{free})] \times 100 \quad (1)$$

where ΔW_{free} and ΔW_{inh} are the weight losses of metal per unit area in the absence and presence of the investigated pharmaceutical compounds at given time period and temperature, respectively.

2.2.2. Electrochemical measurement

Three electrochemical techniques, namely potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM), were used to study the corrosion behavior. All experiments were conducted in a conventional three-electrode cell assembly at selected temperatures. The carbon steel electrode of size (1x1 cm) and sealed with epoxy resin leaving an exposed area of 1 cm^2 and the rest being covered with extra pure paraffin wax was used as working electrode. The cell consisted of a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was polished successively with different grades of emery paper, washed with bidistilled water and then degreased with acetone. All the tests were carried out under unstirred conditions without deaeration.

All the electrochemical studies were performed using Gamry Instrument Series G 750™ Potentiostat/Galvanostat/ZRA with Gamry applications include software DC105 for potentiodynamic measurements, software EIS300 for EIS measurements, and EFM140 to calculate the corrosion current density and the Tafel constants for EFM measurements. A personal computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data.

The working electrode was immersed in the solutions and the constant steady-state (open circuit) potential was recorded when it became virtually constant. Tafel curves were obtained by changing the electrode potential automatically from -1200 to +200 mV with respect to open circuit potential at a scan rate of 5 mV s^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to obtain corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The inhibition efficiency (%IE) and the surface coverage (θ) were calculated using the following relations:

$\%\ IE = \theta \times 100 = [1 - (I_{corr\ (inh)} / I_{corr\ (free)})] \times 100$ (2)

where $I_{corr\ (free)}$ and $I_{corr\ (inh)}$ are the corrosion current densities in the absence and presence of the investigated pharmaceutical compounds, respectively.

EIS measurements were carried out in a frequency range of 100 kHz to 100 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential.

The inhibition efficiency (%IE) of the inhibitor has been found out from the charge transfer resistance values using the following Eq. (3) [4]:

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

where R^{o}_{ct} and R_{ct} are the charge transfer resistance in the presence and of absence of the investigated pharmaceutical compounds, respectively.

The interfacial double layer capacitance (C_{dl}) values were obtained [5] by determining the frequencies at which the imaginary component of the impedance is maximum f ($-Z''_{max}$), using the following equation:

$C_{dl} = Y_o (\omega_{max})^{n-1}$ (4)

where Y_o is the CPE coefficient, (ω_{max}) is the frequency at which the imaginary part of impedance ($-Z_i$) has a maximum and (n) is the CPE exponent (phase shift).

EFM can be used as a rapid and non destructive technique for corrosion rate measurements without prior knowledge of Tafel constants. EFM carried out using two frequencies 20 and 50 mHz. The base frequency was 0.1 Hz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 20 and 50 mHz. Equilibrium time leading to steady state of the specimens was 30 min. $\%\ IE_{EFM}$ calculated from Eq. (5) was calculated using the following equation:

$\%\ IE_{EFM} = [1 - (I_{corr\ (inh)} / I_{corr\ (free)})] \times 100$ (5)

where $I_{corr\ (inh)}$ and $I_{corr\ (free)}$ as before.

2.2.3 Scanning electron microscopy

The carbon steel specimen immersed in various test solutions for 3 days were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out using scanning electron microscopy (SEM) and EmissiondispersiveX-rayanalysis(EDX) Model HITACHI S-3000H.

2.2.4. Theoretical study

All the quantum chemical calculations were performed using Materials Studio DMol [6]version 4.4.0. The following quantum chemical indices were considered: HOMO energy (highest occupied molecular orbital), LUMO energy (lowest unoccupied molecular orbital), dipole moment (μ), energy gap, ΔE ($\Delta E = E_{LUMO} - E_{HOMO}$) and Mulliken charge of the investigated pharmaceutical compounds.

3. Results and Discussion

3.1. Weight loss measurements

The weight loss-time curves of carbon steel with the addition of Actonel in 0.5 M HCl at various concentrations is shown in Figure (1), (similar curves were obtained in presence of the other inhibitors, but not shown). The curves of Fig. 1 shows that the weight loss values of carbon steel in 0.5 M HCl solution containing Actonel decrease as the concentration of the inhibitor increases; i.e., the corrosion inhibition strengthens with the inhibitor concentration, this is appear in the Table (3).This trend may result from the fact that the adsorption of inhibitor on the carbon steel increases with the inhibitor concentration thus the carbon steel surface is efficiently separated from the medium by the formation of a film on its surface**[7,8].** The order of inhibition efficiency obtained from Weight loss measurements is as follows: Actonel >Fosamax >Etidron

Table (1) Chemical composition (weight %) of the carbon steel

Chemical Constituent	C	Mn	P	Si	Fe
Composition (wt %)	0.2	0.6	0.04	0.003	Rest

Table (2) Names, molecular structures, molecular weights and molecular formulas of pharmaceutical drugs

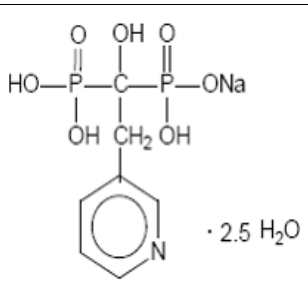
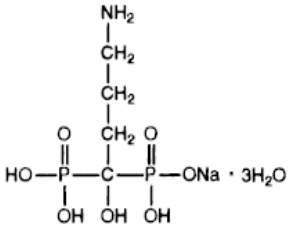
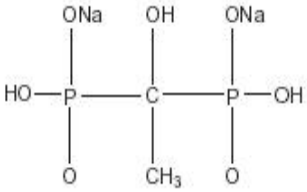
Names	Structures	Molecular Weights	Molecular Formulas
Actonel (Risedronate sodium)		350.13	$C_7H_{10}NO_7P_2Na•5/2\ H_2O$
Fosamax (Alendronate sodium)		325.12	$C_4H_{12}NO_7P_2Na•3H_2O$
Etidron (Etidronate disodium)		250.00	$C_2H_6O_7P_2\ Na_2$

Table (3) Data of weight loss measurements for carbon steel in 0.5 M HCl solution in the absence and presence of different concentrations of the investigated pharmaceutical compounds at 25°C

Compound	Conc., M	CR mg cm^{-2} min^{-1}	% IE
Blank	0.5M HCl	0.0040	---------
Actonel	1×10^{-6}	0.0016	78.3
	5×10^{-6}	0.0015	80.3
	9×10^{-6}	0.0012	82.2
	13×10^{-6}	0.0011	85.4
	17×10^{-6}	0.0008	86.6
	21×10^{-6}	0.0007	91.4
Fosamax	1×10^{-6}	0.0017	73.2
	5×10^{-6}	0.0015	75.8
	9×10^{-6}	0.0014	77.7
	13×10^{-6}	0.0012	81.5

	17 x 10^{-6}	0.0010	84.7
	21 x 10^{-6}	0.0008	87.3
Etidron	1 x 10^{-6}	0.0019	67.9
	5 x 10^{-6}	0.0018	71.4
	9 x 10^{-6}	0.0017	74.3
	13 x 10^{-6}	0.0014	75.0
	17 x 10^{-6}	0.0012	80.7
	21 x 10^{-6}	0.0010	85.0

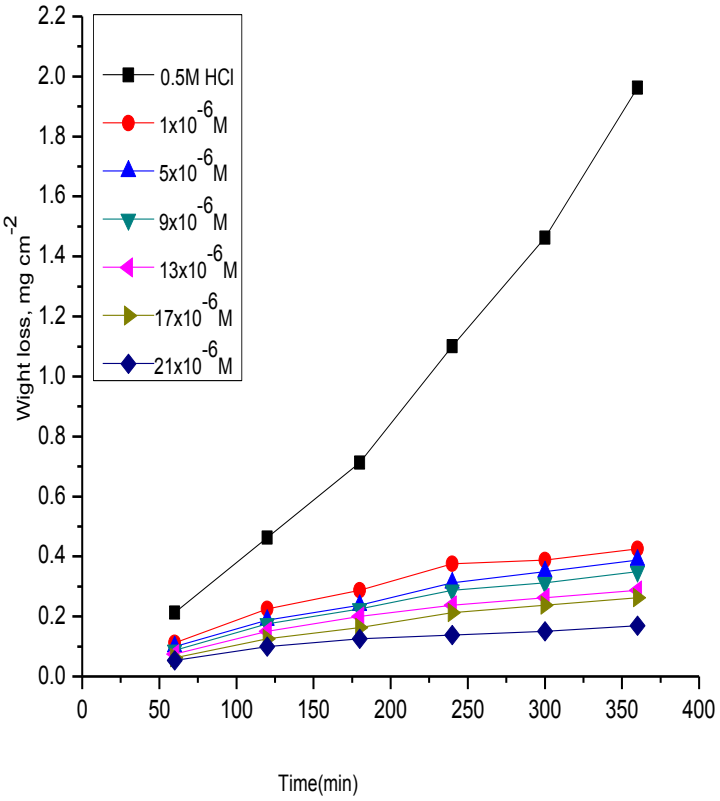


Figure (1) Weight loss-time curves of carbon steel in 0.5 M HCl in the absence and presence of various concentrations of the investigated actonel at 25°C

3.1.1. Adsorption isotherm

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system [9]. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the investigated pharmaceutical compounds in 0.5 M HCl solution. Attempts were made to fit (θ) values to various adsorption isotherms. The Langmuir's adsorption isotherm fits well the experimental data. Plots of (C/ θ) vs. (C) for all concentrations of pharmaceutical compounds. Figure (2) a straight line relationship in all cases was obtained. This suggests that the adsorption of inhibitors on the carbon steel surface

follow Langmuir's isotherm. It is well known that the standard adsorption free energy ($\Delta G°_{ads}$) is related to equilibrium constant of adsorption (K_{ads}) and ($\Delta G°_{ads}$) can be calculated by Eq. (6) [10]:

$K_{ads} = 1/55.5 \exp [-\Delta G°_{ads}/RT]$ (6)

Figure (2) represents the plot of (C/ θ) vs. (C) for investigated pharmaceutical drugs. As can be seen from Figure (2), the Langmuir's isotherm is the best one which explains the experimental results. These results confirm the assumption that, these pharmaceutical drugs are adsorbed on the metal surface through the lone pair of electrons of hetero atoms. In addition to, the extent of inhibition is directly related to the performance of adsorption layer which is a sensitive function of the molecular structure. The ($\Delta G°_{ads}$) and (K_{ads}) values for pharmaceutical drugs were calculated and are recorded in Table (4). The high negative values of ($\Delta G°_{ads}$) indicate that these compounds are strongly adsorbed (chemisorption) on carbon steel surface at all the temperature ranges studied but the adsorption decreases with the increase in temperature. The negative values of ($\Delta G°_{ads}$) ensure that spontaneity of the adsorption process and the stability of adsorbed layer on the carbon steel surface. The high values of (K_{ads}) indicate the strong adsorption of these compounds on carbon steel surface. These values were found to run parallel to the % IE (Actonel > Fosamax > Etidron). This result reflects the increasing capability, due to structural formation, on the metal surface [11].

Table (4) Thermodynamic parameters for the adsorption of the investigated pharmaceutical compounds in 0.5 M HCl on the carbon steel at temperature 25 °C

Inhibitor	K_{ads} x10^{-4} M^{-1}	Slope	R^2	$-\Delta G°_{ads}$ kJ mol^{-1}
Actonel	66.55	1.19	0.98677	43.2
Fosamax	57.40	1.24	0.98506	42.8
Etidron	45.97	1.27	0.97344	42.3

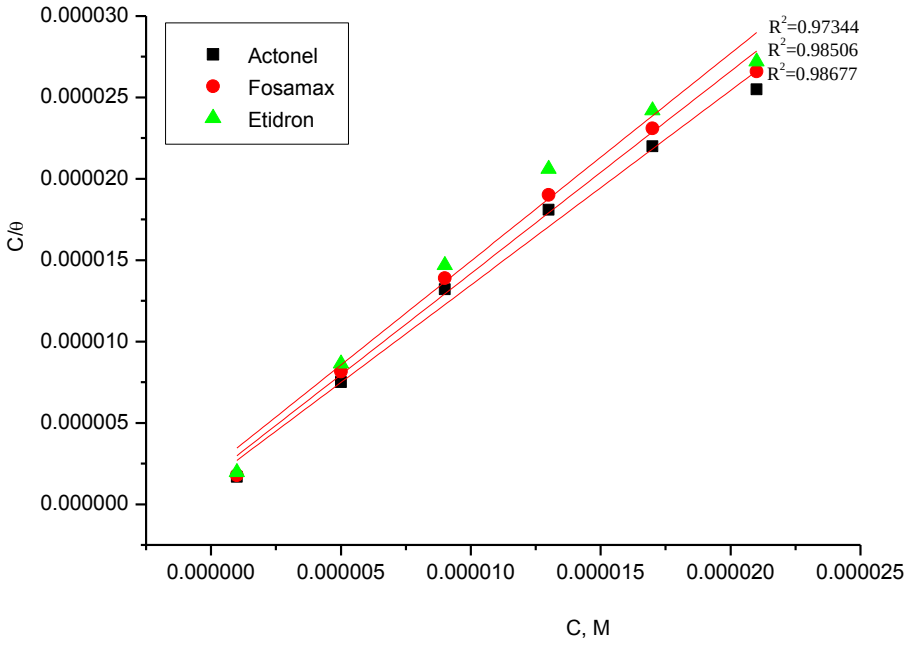


Figure (2) Langmuir adsorption isotherm for investigated pharmaceutical compoundsfor corrosion of carbon steel in 0.5 M HCl at 25°C

3.1.2. Effect of temperature

The effect of temperature on the rate of corrosion of carbon steel in 0.5 M HCl containing different concentration from investigated pharmaceutical compounds was tested by weight loss measurements over a temperature range from 25 to 55 ^{o}C.The effect of increasing temperature on the corrosion rate and IE obtained from weight loss measurements. The results revealed that, the rate of corrosion increases as the temperature increases and decreases as the concentration of these compounds increases for all compound used. The activation energy (E^{*}_{a}) of the corrosion process was calculated using Arrhenius equation:

$k = A \exp(-E_a^{*} / RT)$ (7)

where k is the rate of corrosion, A is the Arrhenius constant, R is the gas constant and T is the absolute temperature.

Table (5) Thermodynamic activation parameters for the dissolution of carbon steel in 0.5 M HCl in the absence and presence of different concentrations of the investigated pharmaceutical compounds.

Inhibitor	Conc., M	E_a^{*} kJ mol^{-1}	ΔH^{*} kJ mol^{-1}	$-\Delta S^{*}$ J mol^{-1} K^{-1}
blank	0.0	38.7	17.9	113.7
Actonel	1 x 10^{-6}	45.9	21.1	96.8
	5 x 10^{-6}	46.2	21.2	96.9
	9 x 10^{-6}	47.5	21.8	93.5
	13 x 10^{-6}	48.5	22.2	91.4
	17 x 10^{-6}	49.6	22.7	90.0
	21 x 10^{-6}	50.7	23.1	87.8
Fosamax	1 x 10^{-6}	44.7	20.5	100.2
	5 x 10^{-6}	45.2	20.8	99.2
	9 x 10^{-6}	46.6	21.1	98.8
	13 x 10^{-6}	47.7	21.4	95.9
	17 x 10^{-6}	48.6	22.2	91.4
	21 x 10^{-6}	50.0	22.8	88.8
Etidron	1 x 10^{-6}	43.6	20.1	102.9
	5 x 10^{-6}	44.5	20.4	101.0
	9 x 10^{-6}	45.4	20.8	98.7
	13 x 10^{-6}	46.0	21.1	97.5
	17 x 10^{-6}	47.0	21.6	95.6
	21 x 10^{-6}	49.5	22.6	88.4

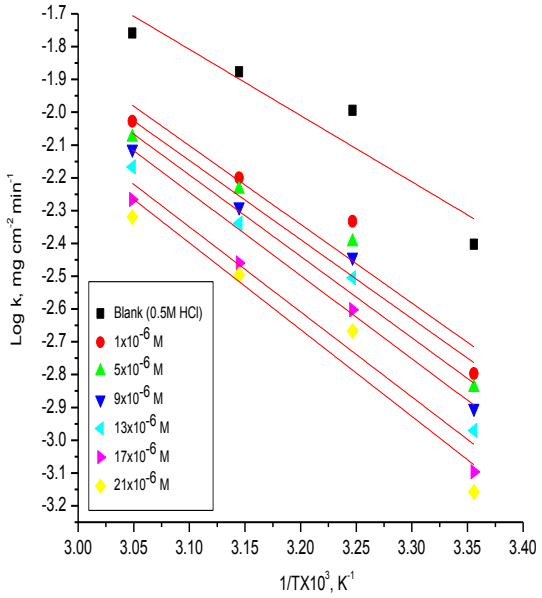


Figure (3) Arrhenius plots (log k vs. 1/ T) for corrosion of carbon steel in 0.5 M HCl in the absence and presence of different concentrations of actonel

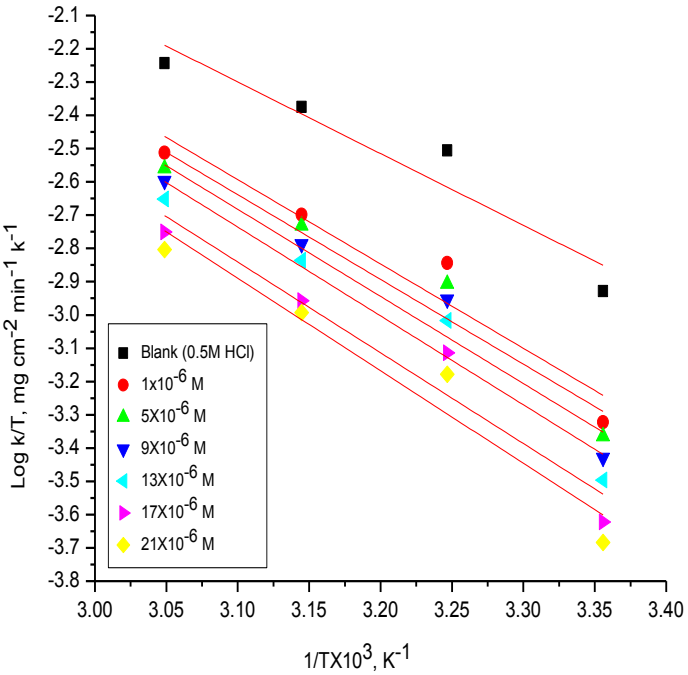


Figure (4) Plots of (log k / T) vs. 1/ T for corrosion of carbon steel in 0.5 M HCl in the absence and presence of different concentrations of actonel

Figure (3) present the Arrhenius plot in the presence and absence of Actonel drug (similar curves were obtained in presence of the other inhibitors, but not shown). E^*_a values determined from the slopes of these linear plots are shown in Table (5) which showed that the value of E^*_a for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of carbon steel is slow in the presence of inhibitor and can be interpreted as due

to physical adsorption[12]. It is known from Eq. (7) that the higher E^*_a values lead to the lower corrosion rate. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion[13]. Enthalpy and entropy of activation (ΔH^*, ΔS^*) of the corrosion process were calculated from the transition state theoryTable (5):

$k = (k'/ Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$ (8)

where h is Planck's constant, k' is the Boltzmann constant and N is Avogadro's number

A plot of log (k/ T) vs. 1/ T for carbon steel in 0.5 HCl at different concentrations from investigated compounds, give straight lines as shown in Figure (4) for Actonel drug (similar curves were obtained in presence of the other drugs, but not shown). The positive signs of ΔH^* reflect the endothermic nature of the carbon steel dissolution process. 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[14].The order of the inhibition efficiencies of these investigated pharmaceutical drugs as gathered from the increase in E_a^* and ΔH^* values and decrease in ΔS^* values are as follows: Actonel >Fosamax >Etidron

3.2 Potentiodynamic polarization technique

Figure (5) shows the anodic and cathodic Tafel polarization curves for carbon steel in 0.5 M HCl in the absence and presence of varying concentrations of inhibitor Actonel at 25°C respectively (similar curves were obtained in presence of the other pharmaceutical inhibitors, but not shown). From Figure (5), it is clear that both anodic metal dissolution and cathodic H_2 reduction reactions were inhibited when investigated inhibitors were added to 0.5 HCl and this inhibition was more pronounced with increasing inhibitor concentration. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors. This behavior indicates that the undertaken additives act as mixed-type inhibitors **(15, 16)**. The results show that the increase in inhibitor concentration leads to decrease the corrosion current density (I_{corr}), but the Tafel slopes (β_a ,β_c) ,are approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) were affected without changing the dissolution mechanism **(17-19).**The % IE obtained from EIS measurements are close to those deduced from weight loss measurements. The order of inhibition efficiency obtained from Potentiodynamic polarization technique measurements is as follows: Actonel >Fosamax >Etidron

Table (6): Data from potentiodynamic polarization of carbon steel in 0.5 M HCl containing various concentrations of pharmaceutical compounds Actonel, Fosamax & Etidron at 25°C

Inhibitor	Conc., M	- $E_{corr.}$ mV(vs SCE)	$I_{corr.}$ mA cm^{-2}	β_a mV dec^{-1}	β_c mVdec^{-1}	θ	% IE
Blank	0.5M HCl	510.9	9.395	470.7	398.7	-	-
Actonel	$1x10^{-6}$	533.2	3.329	336.6	289.5	0.646	64.6
	$5 x10^{-6}$	532.7	2.764	307.6	262.8	0.706	70.6
	$9 x10^{-6}$	527.9	2.512	318.2	275.1	0.733	73.3
	$13 x10^{-6}$	537.2	1.858	271.5	243.4	0.802	80.2
	$17 x10^{-6}$	536.7	1.634	265	243.4	0.826	82.6
	$21 x10^{-6}$	527.1	1.195	252.4	221.4	0.873	87.3
Fosamax	$1 x10^{-6}$	-518	3.510	383.7	301.1	0.626	62.6

	5 x10^{-6}	-531.2	3.288	348.4	296.3	0.650	65.0
	9 x10^{-6}	-535.8	2.964	364.8	310.4	0.685	68.5
	13 x10^{-6}	-524.3	2.518	313.7	261.2	0.732	73.2
	17 x10^{-6}	-533.2	1.937	295.3	262.4	0.794	79.4
	21 x10^{-6}	-524.8	1.430	287.3	249.1	0.848	84.8
Etidron	1 x10^{-6}	-535.3	3.892	354.9	308	0.586	58.6
	5 x10^{-6}	-515.8	3.410	371.5	304.5	0.637	63.7
	9 x10^{-6}	-522.4	3.117	363.8	300.1	0.668	66.8
	13 x10^{-6}	-517	2.611	332.8	265.8	0.722	72.2
	17 x10^{-6}	-515.8	2.329	336.8	272.3	0.752	75.2
	21 x10^{-6}	-519.6	1.549	290.7	244.4	0.835	83.5

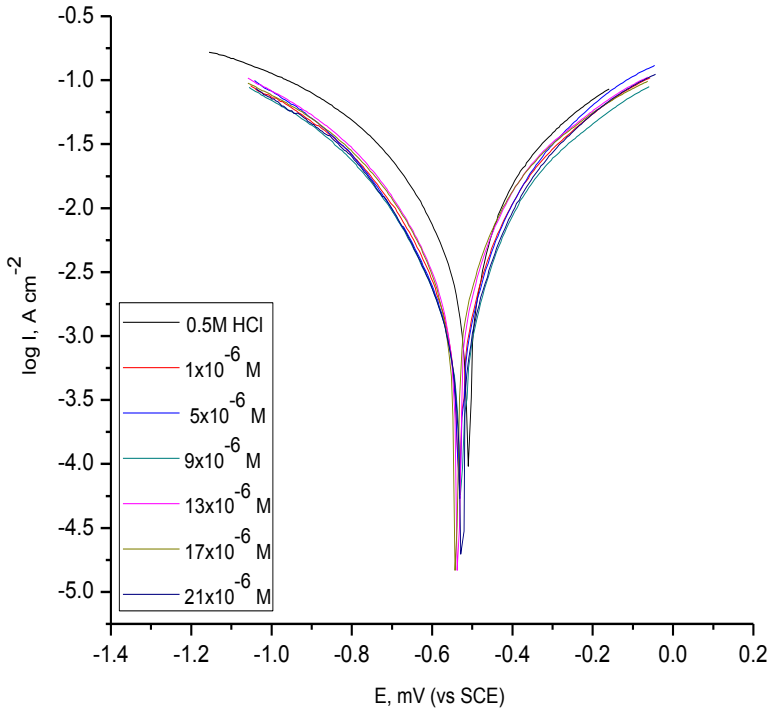


Figure (5): Potentiodynamic polarization curves for corrosion of carbon steel in 0.5 HCl in the absence and presence of different concentrations of Actonel at 25 ^{0}C

3.3-Electrochemical impedance spectroscopy (EIS)

The effect of inhibitor concentration on the impedance behavior of carbon steel in 0.5 M HCl solution at 25^0C is presented in Figure (6-A). The curves show a similar type of Nyquist plots for carbon steel in the presence of various concentrations of Actonel;similar curves were obtained for other inhibitors but not shown. 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 [**20, 21]**.

Table (7): EIS data of carbon steel in 0.5 M HCl and in the absence and presence of different concentrations of pharmaceutical compounds at 25 °C

Comp.	Conc., M	C_{dl}, μFcm^{-2}	R_{ct}, $\Omega\ cm^2$	θ	% IE
Blank	0.5 M HCl	97.97	14.36	-	-
Actonel	1×10^{-6}	116.60	42.53	0.662	66.2
	5×10^{-6}	140.35	56.05	0.744	74.4
	9×10^{-6}	94.43	74.29	0.807	80.7
	13×10^{-6}	133.35	108.2	0.867	86.7
	17×10^{-6}	71.77	133.8	0.893	89.3
	21×10^{-6}	87.20	242	0.941	94.1
Fosamax	1×10^{-6}	115.64	37.11	0.613	61.3
	5×10^{-6}	102.14	51.55	0.721	72.1
	9×10^{-6}	93.22	65.94	0.782	78.2
	13×10^{-6}	297.30	81.61	0.824	82.4
	17×10^{-6}	158.83	122.1	0.882	88.2
	21×10^{-6}	145.20	161.5	0.911	91.1
Etidron	1×10^{-6}	84.67	29.84	0.519	51.9
	5×10^{-6}	126.04	33.55	0.572	57.2
	9×10^{-6}	70.79	47.85	0.700	70.0
	13×10^{-6}	91.83	66.91	0.785	78.5
	17×10^{-6}	48.08	87.01	0.834	83.4
	21×10^{-6}	171.49	126	0.886	88.6

Inspections of the data reveal that each impedance diagram consists of a large capacitive loop with one capacitive time constant in the Bode–phase plots Figure (6-B). The electrical equivalent circuit model is shown in Figure (7). It used to analyze the obtained impedance data. The model consists of the solution resistance (R_s), the charge-transfer resistance of the interfacial corrosion reaction (R_{ct}) and the double layer capacitance (C_{dl}). Excellent fit with this model was obtained with our experimental data. EIS data Table (7) show that the (R_{ct}) values increases and the (C_{dl}) values decreases with increasing the inhibitor concentrations. 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 **[22, 23]** 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 **[24]** The % IE obtained from EIS measurements are in good agreement with that obtained from weight loss and potentiodynamic polarization measurements. The order of inhibition efficiency obtained from EIS measurements is as follows: Actonel >Fosamax >Etidron

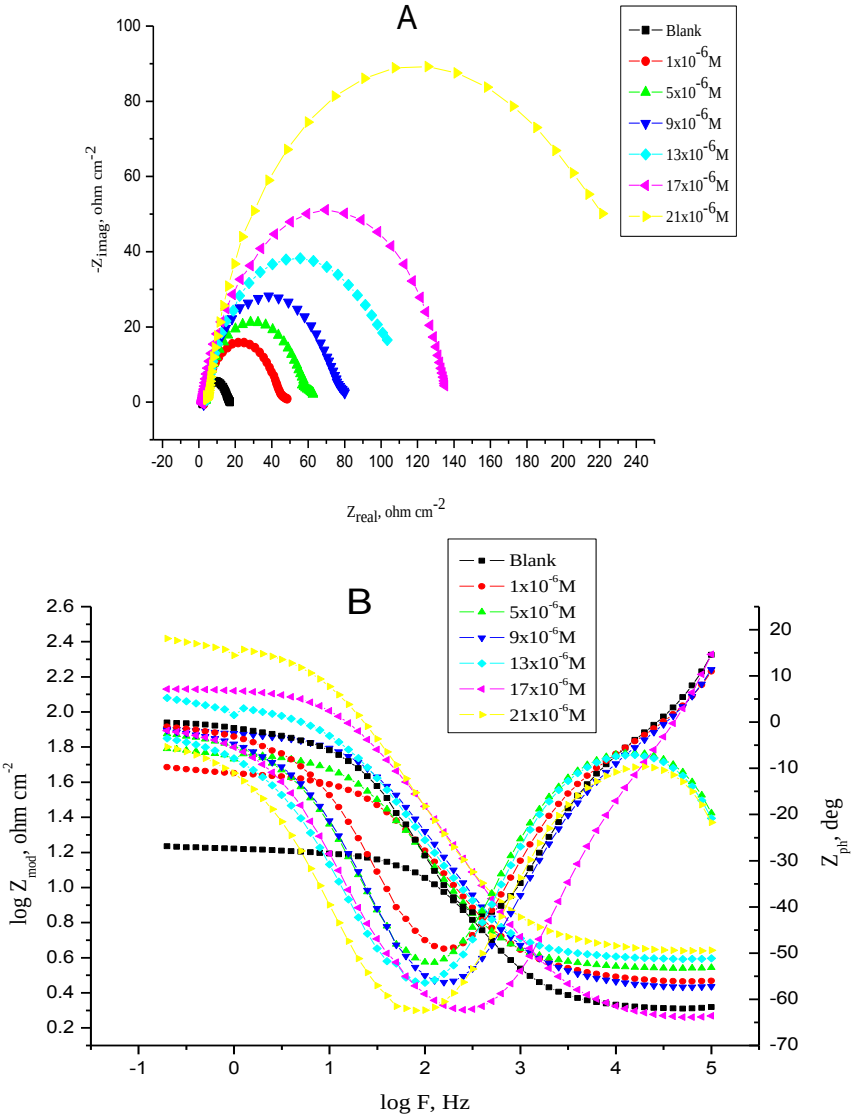


Figure (6): The Nyquist (A) and Bode (B) plots for corrosion of carbon steel in 0.5 M HCl in the absence and presence of different concentrations of Actonel at 25°C

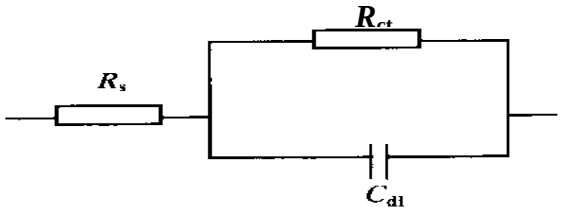


Figure (7): Electrical equivalent circuit model used to fit the results of impedance

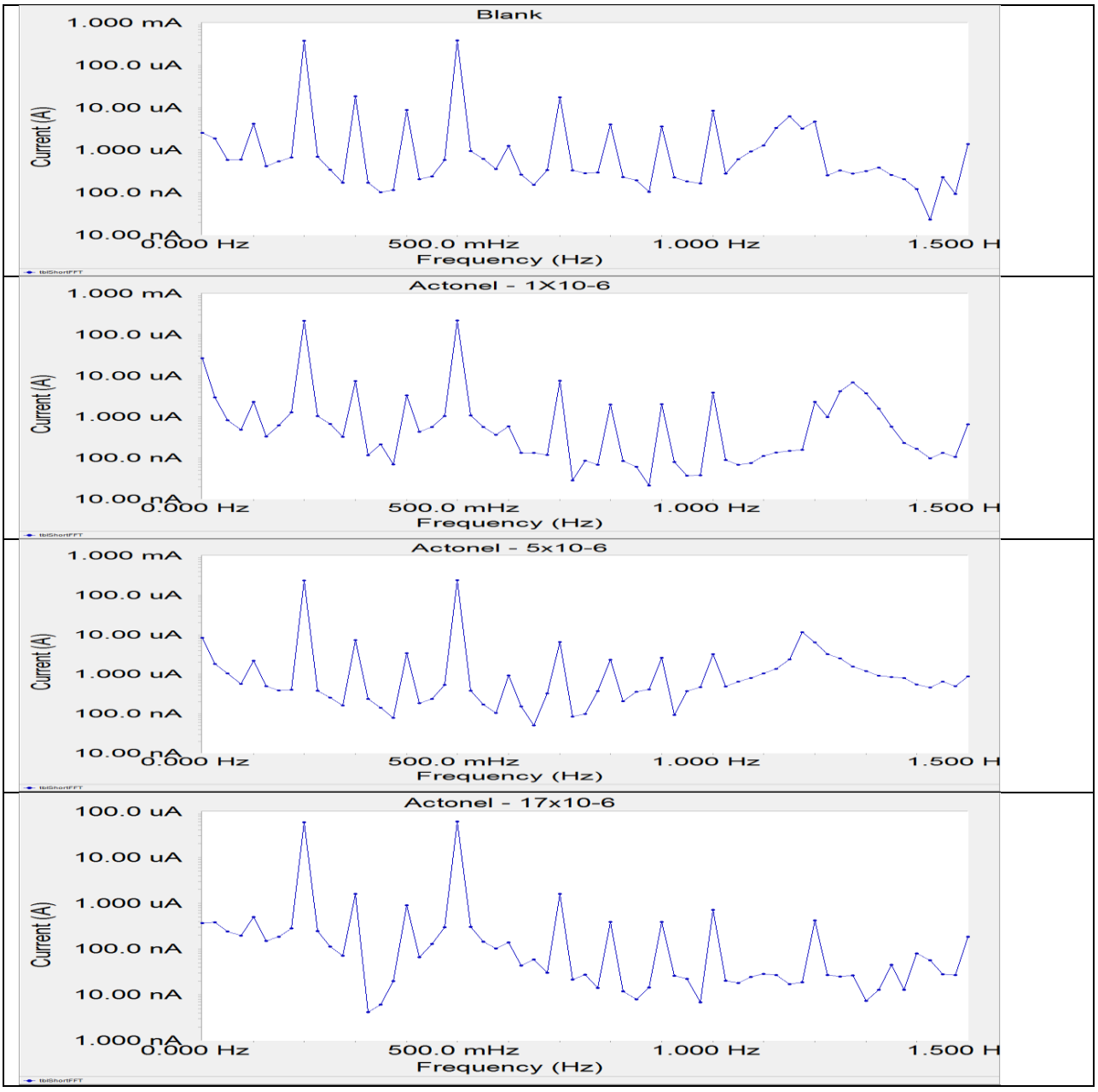
3.4. Electrochemical frequency modulation measurements

In corrosion research, it is known that the corrosion process is non-linear in nature, a potential distortion by one or more sine waves will generate responses at more frequencies than the frequencies of applied signal. Virtually no attention has been given to the inter modulation or electrochemical frequency modulation. However, EFM showed that this non-linear response contains enough information about the corroding system so that the corrosion current can be calculated directly. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement. With the causality factors the experimental EFM data can be verified. Figures (8) show 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 larger peaks were used to calculate the corrosion current density (I_{corr}), the Tafel slopes (β_a and β_C) and

Table (8): Electrochemical kinetic parameters obtained by EFM technique for carbon steel in the absence and presence of various concentrations of investigated pharmaceutical compounds in 0.5 M HCl at 25 °C

Comp.	Conc., M	I_{corr} μAcm^{-2}	β_c $mVdec^{-1}$	β_a $mVdec^{-1}$	CF-2	CF-3	θ	% IE
Blank	0.5 M HCl	671	98.4	138.0	2.073	3.1	-	-
Actonel	1×10^{-6}	398.5	105.3	135.3	2.082	3.273	0.406	40.6
	5×10^{-6}	358.0	90.0	107.2	2.099	3.134	0.467	46.7
	9×10^{-6}	273.7	30.0	33.8	2.128	2.957	0.592	59.2
	13×10^{-6}	197.3	114.5	119.8	2.116	3.152	0.706	70.6
	17×10^{-6}	129.1	125.4	157.6	1.986	2.919	0.808	80.8
	21×10^{-6}	76.1	99.5	134.7	1.856	2.995	0.887	88.7
Fosamax	1×10^{-6}	434.7	95.9	137.1	2.029	3.099	0.352	35.2
	5×10^{-6}	375.4	111.5	118.7	2.004	3.089	0.441	44.1
	9×10^{-6}	313.3	101.6	144.0	2.045	2.963	0.533	53.3
	13×10^{-6}	223.8	94.2	123.3	2.039	3.646	0.667	66.7
	17×10^{-6}	150.0	100.7	129.0	1.899	3.023	0.777	77.7
	21×10^{-6}	98.04	92.1	128.5	2.066	2.982	0.854	85.4
Etidron	1×10^{-6}	463.0	59.7	65.3	1.992	3.183	0.310	31.0
	5×10^{-6}	393.2	101.1	117.1	2.03	3.04	0.414	41.4
	9×10^{-6}	327.6	98.7	147.7	2.04	3.180	0.512	51.2
	13×10^{-6}	233.1	20.8	29.7	1.986	3.095	0.653	65.3
	17×10^{-6}	175.5	94.3	108.5	2.132	3.163	0.739	73.9
	21×10^{-6}	119.7	65.4	73.2	2.108	3.103	0.822	82.2

thecausality factors(CF-2 and CF-3).These electrochemical corrosion kinetic parameters at different concentrations of the investigated (I_{corr}),the Tafel slopes (β_a and β_C) and thecausality factors(CF-2 and CF-3).These electrochemical corrosion kinetic parameters at different concentrations of the investigated pharmaceutical drugs in 0.5 M HCl at 25ºC were listed in Table (8). The inhibition efficiency % IE increasesby increasing the studied inhibitor concentrations. The causality factors CF-2 and CF-3 are close to their theoretical values of 2.0 And 3.0, respectively indicating that the measured data are of good quality. The calculated inhibition efficiency obtained from weight loss, potentiodynamic polarization and EIS measurements are in good agreement with that obtained from EFM measurements. The order of inhibition efficiency obtained from EIS measurements is as follows: Actonel >Fosamax>Etidron



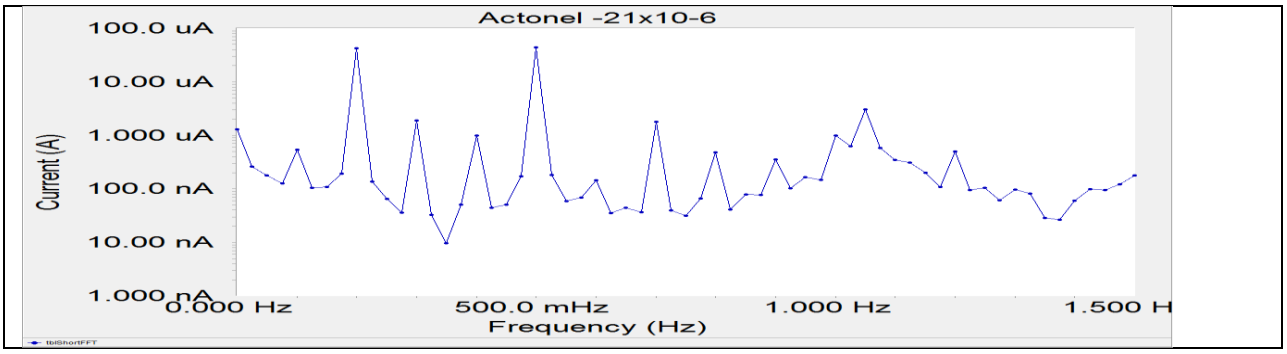


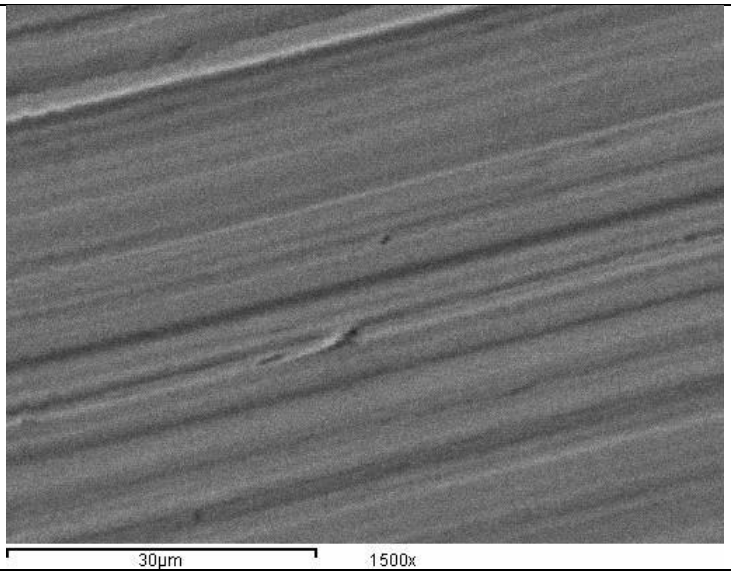
Figure (8): EFM spectra for carbon steel in the absence and presence of different concentrations of Actonel in 0.5 M HCl

3.5. Surface examination using SEM–EDX techniques

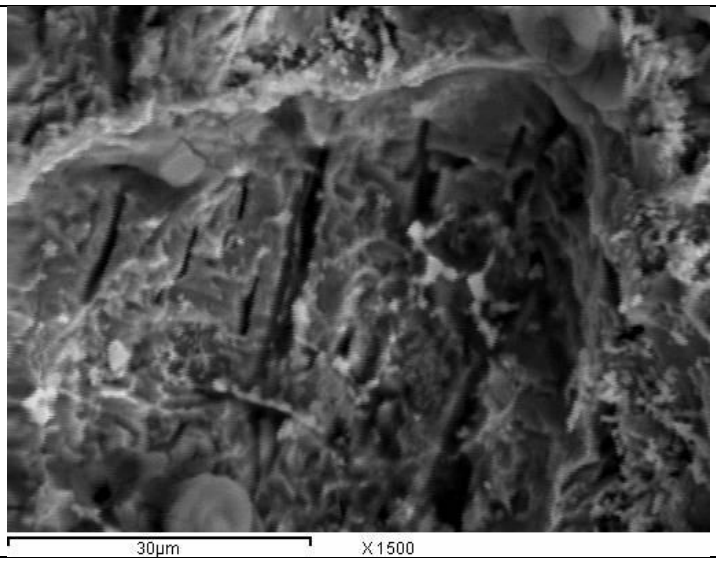
3.5.1. Scanning Electron Microscopy (SEM) technique

Figure (9) represents the micrographic obtained for carbon steel samples in presence and in absence of 21x 10^{-6} M from the investigated pharmaceutical drugs after exposure for 3 days immersion. It is clear that carbon steel surfaces suffer from severe corrosion attack in the blank sample. It is important to stress out that when the compound is present in the solution, the morphology of carbon steel surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the carbon steel. This may be interpreted as due to the adsorption of the investigated pharmaceutical drugs on the carbon steel surface incorporating into the passive film in order to block the active site present on the carbon steel surface. Or due to the involvement of inhibitor molecules in the interaction with the reaction sites of carbon steel surface, resulting in a decrease in the contact between carbon steel and the aggressive medium and sequentially exhibited excellent inhibition effect [25, 26].

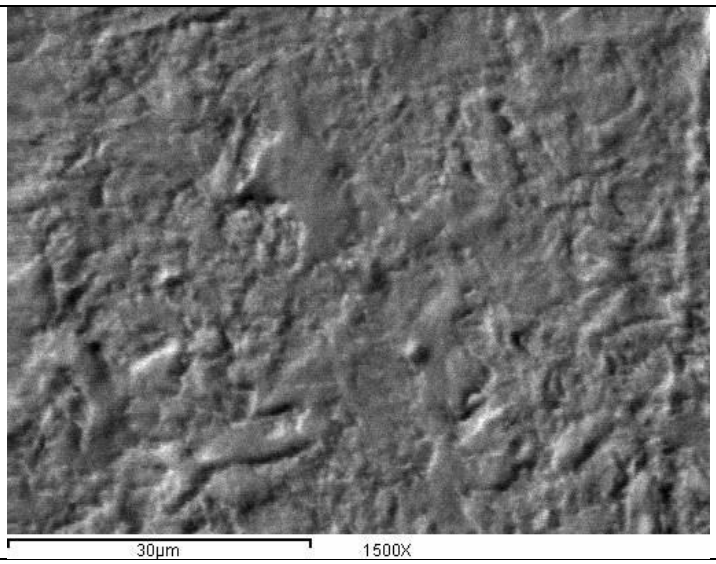
Pure carbon steel



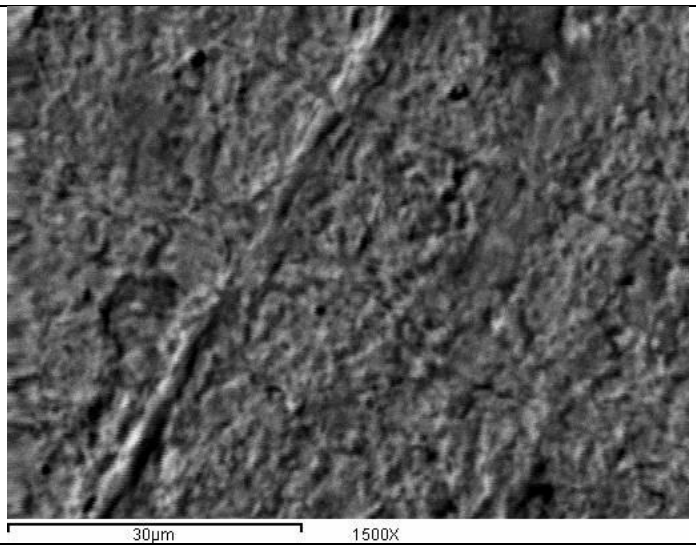
blank



Actonel



Fosamax



Etidron

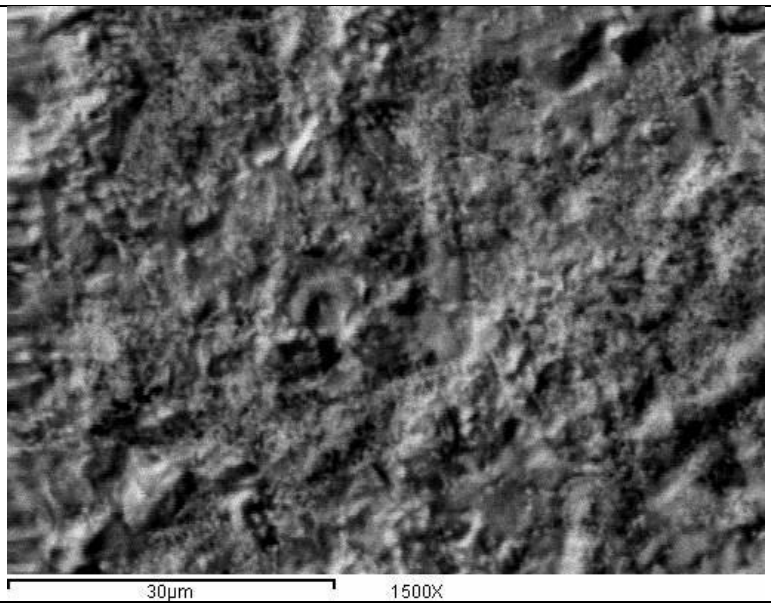


Figure (9)SEM micrographs for carbon steel in absence and presence of 21 x 10^{-6} M of the investigated pharmaceutical drugs

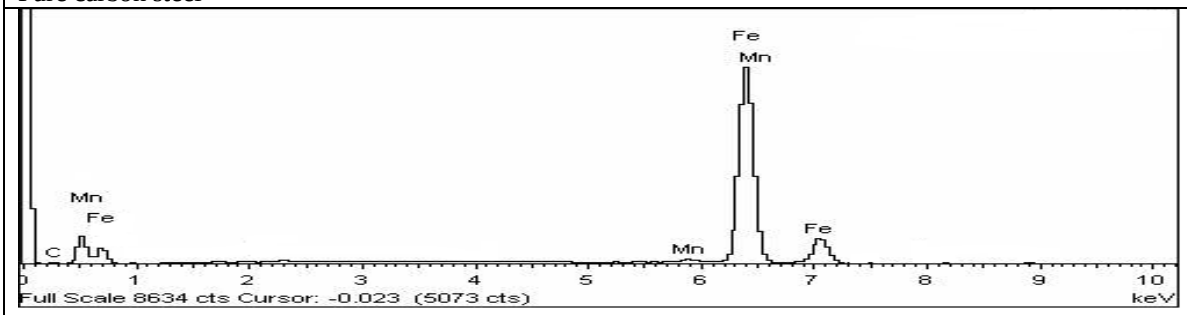
3.5.2. Emission dispersive X-ray analysis (EDX)

Surface analyses were carried out using emission dispersive x-ray analysis EDX. The results were shown in Figures (10) represent the various peaks owing to different elements. From all analysis charts, it was found that the results of EDX may be explained and discussed depending on the values of weight percentages wt% of carbon and chloride atoms on the surface as follow:

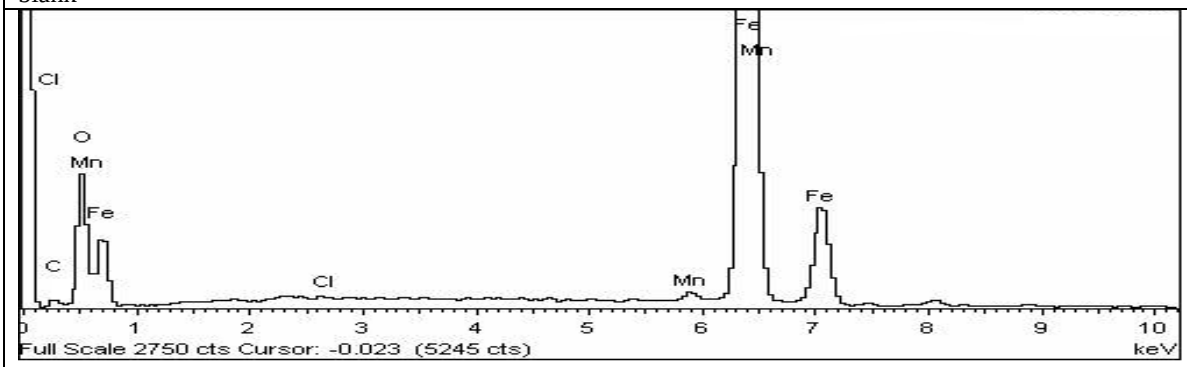
1) In all the charts of EDX the carbon atom peak appears around the value of 0.2 KV and the peak of chloride atom appears at 2.6 KV. As the corrosive medium is 0.5 M HCl solution and the investigated pharmaceutical drugs additives consist mainly of C, O, P & N atoms, so the variation of chloride and carbon weight percentages on the surface can be used quantitively to explain the adsorption of the investigated pharmaceutical drugs on the surface of carbon steel.

2) For example, Figure (10-Blank) represents EDX of carbon steel exposed to 0.5 M HCl only at 25^{o}C for three days, where Figure (10-Actonel, Fosamax &Etidron) represents the same sample from carbon steel in the presence of 21x10^{-6} M of Actonel, Fosamax &Etidron respectively. From comparison the weight % value of carbon is 2.36 % for the blank which less than the wt % values of all the investigated pharmaceutical drags Actonel , Fosamax &Etidron .and decreased from 22.04 % in Actonel to 2.88 % in Etidron, on the other hand the weight % value of chloride in blank is 0.44% greater than the weight % values of all the investigated pharmaceutical drags Actonel , Fosamax &Etidron .and increased from 0.31 % in Actonel to 0.41 % in Etidron. This is due to the replacement of the firstly adsorbed chloride atoms which comes from the corrosive medium by C atoms that comes from the investigated pharmaceutical drugs. These results confirm the adsorption of the investigated pharmaceutical drugs on the surface of carbon steel. Wholly.

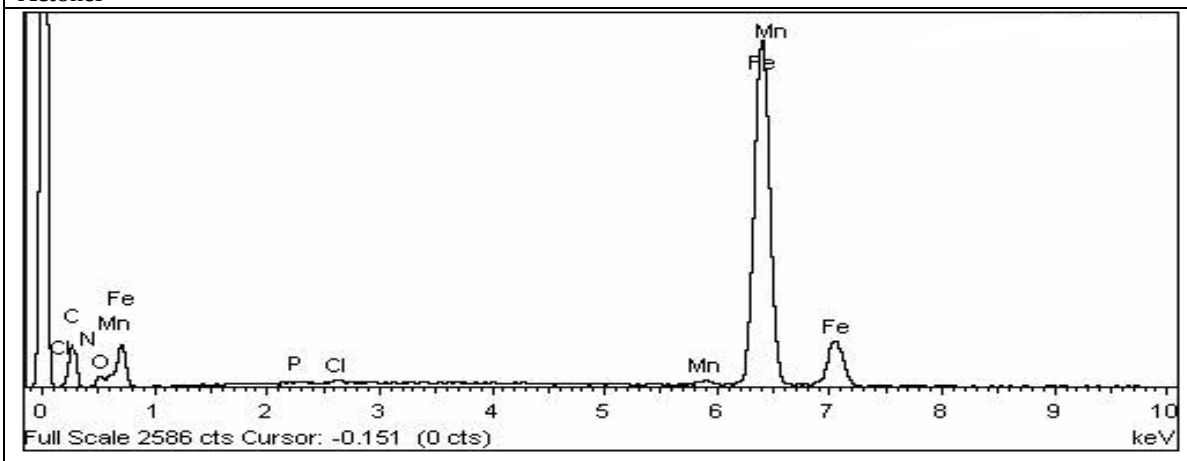
Pure carbon steel



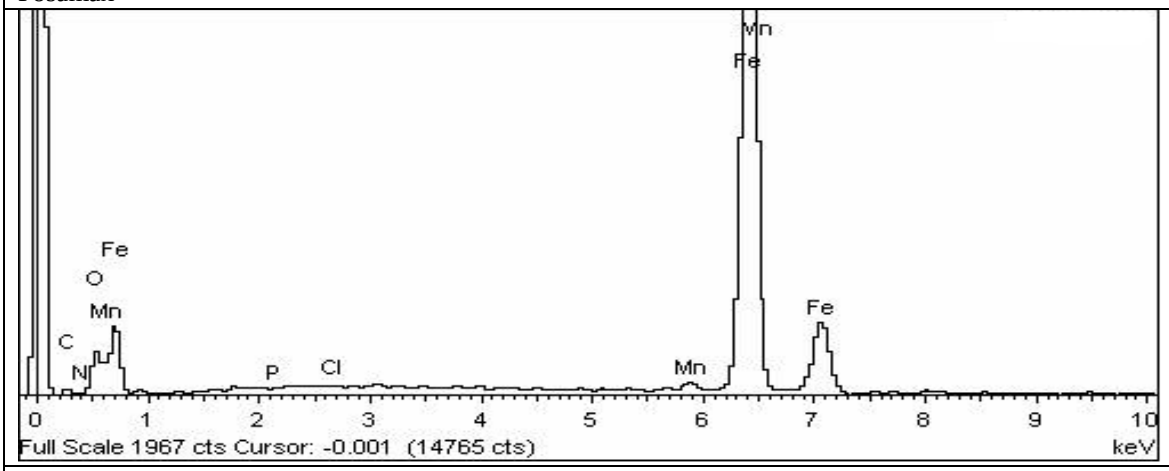
blank



Actonel



Fosamax



Etidron

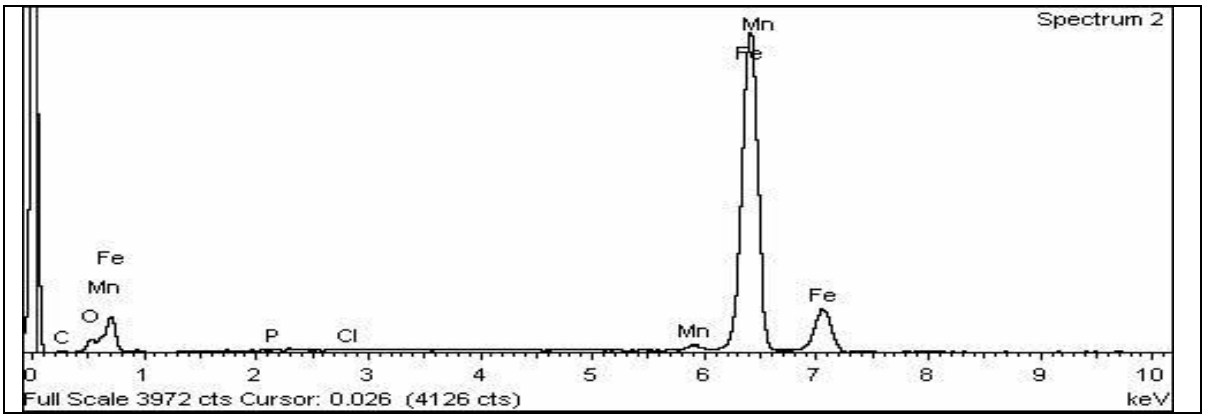


Figure (10): EDX analysis on carbon steel in the presence and absence of the investigated pharmaceutical drugs for 3 days immersion

Table (9): Surface composition (weight %) of carbon steel after 3h of immersion in HCl without and with the optimum concentrations of the studied drugs

(Mass %)	Fe	Mn	C	O	N	Cl	P
Pure	96.72	0.76	2.52	-	-	-	-
blank	56.83	0.61	2.34	39.81	-	0.44	-
Actonel	60.64	0.56	22.04	13.83	2.43	0.31	0.17
Fosamax	62.12	0.63	18.40	16.21	2.21	0.36	0.13
Etidron	70.97	0.76	2.88	5.82	2.14	0.411	0.11

3.6.Quantumchemicalcalculationsofthe investigated pharmaceutical drugs

The reactive ability of the inhibitor is related to E_{HOMO}, E_{LUMO} [27]. Higher E_{HOMO} of the adsorbent leads to higher electron donating ability [28]. Low E_{LUMO} indicates that the acceptor accepts electrons easily. The calculated quantum chemical indices (E_{HOMO}, E_{LUMO}, μ) of investigated compounds are shown in Table (10). The difference $\Delta E = E_{LUMO} - E_{HOMO}$ is the energy required to move an electron from HOMO to LUMO. Low ΔE facilities adsorption of the molecule and thus will cause higher inhibition efficiency.

The bond gap energy (ΔE) increases from actonel to Etidron. This fact explains the decreasing inhibition efficiency in this order: Actonel>Fosamax>Etidron. Table (10) and Figure (11) show the optimized structures of the three investigated pharmaceutical drugs. So, the calculated energy gaps show reasonably good correlation with the efficiency of corrosion inhibition. Table (10) also indicates that (Actonel) possesses the lowest total energy that means that compound (Actonel) adsorption occurs easily and is favored by the highest softness. The HOMO and LUMO electronic density distributions of these molecules were plotted in Figure (11) The data presented in Table (10) show that the calculated dipole moment decrease from Actonel>Fosamax>Etidron. Alsothisagreeswiththepreviously mentioned experimentaldata.

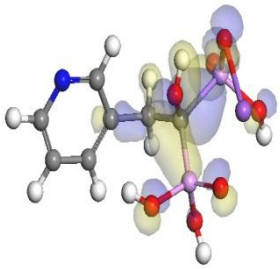
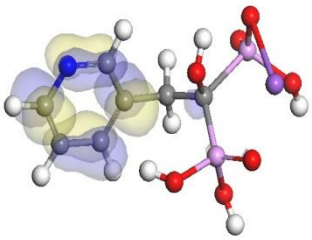
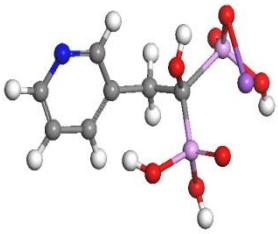
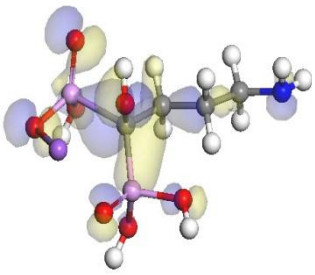
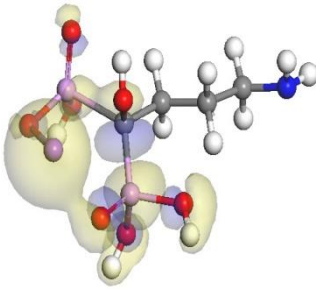
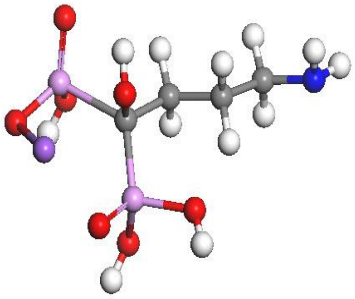
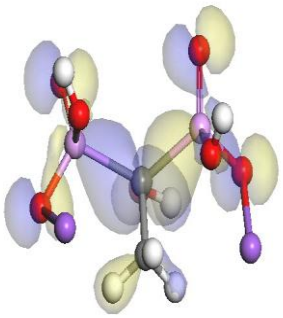
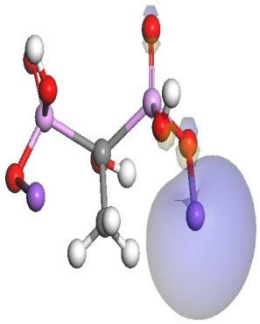
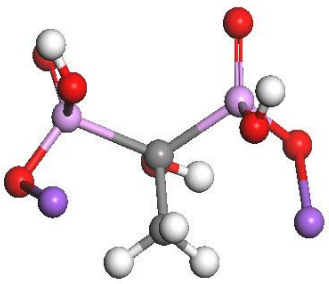
Inhibitors	HOMO	LUMO	Molecular Structure
Actonel			
Fosamax			
Etidron			

Figure (11): the frontier molecular orbital density distribution of the investigated pharmaceutical drugs (HOMO and LUMO)

Table (10) Quantum chemical parameter for investigated pharmaceutical drugs

PM3 liquid phase	$-E_{HOMO}$ (ev)	$-E_{LUMO}$ (ev)	ΔE (ev)	μ Debye)	Molecular surface area A^2
Actonel	8.089	0.338	7.751	3.632	277.461
Fosamax	9.019	0.054	8.965	3.887	267.64
Etidron	9.234	0.138	9.096	14.696	242.145

Mechanism of inhibition

Inhibition of the carbon steel corrosion in 0.5 M HCl by the investigated pharmaceutical drugs as indicated by weight loss, potentiodynamic anodic polarization measurements, Electrochemical Impedance Spectroscopy (EIS), electrochemical frequency modulation method (EFM) and surface examination using SEM–EDX techniques were found to depend on the number of adsorption sites in the molecule and their charge density, molecular size and stability of these additives in acidic solution. The observed corrosion data in presence of these inhibitors, namely: i) The decrease of corrosion rate and corrosion current with increase in concentration of the inhibitor ii) The linear variation of weight loss with time iii) The shift in Tafel lines to higher potential regions iii) The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor molecules takes place iv) The inhibition efficiency was shown to depend on the number of adsorption active centers in the molecule and their charge densities. The corrosion inhibition is due to adsorption of the inhibitors at the electrode/ solution interface, the extent of adsorption of an inhibitor depends on the nature of the metal, the mode of adsorption of the inhibitor and the surface conditions. Adsorption on carbon steel surface is assumed to take place mainly through the active centers attached to the inhibitor and would depend on their charge density. It was concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system. Metals such as carbon steel, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. The order of decreasing the percentage inhibition efficiency of the investigated inhibitors in the corrosive solution was as follow: Actonel >Fosamax>Etidron. Actonel exhibits excellent inhibition power due to: (i) its larger molecular size (350.13) that may facilitate better surface coverage, (ii) its adsorption through 10 centers of adsorption (7-O, 2-P, 1-N atoms) and iii) The lone pair of Cl atom are shared with phenyl group, it becomes a donor by mesomeric effect and increase the electron density on actonel. Fosamax comes after actonel in inhibition efficiency, because it has lesser molecular size (225.12) and have 10 active centres (7-O, 2-P, 1-N atoms) . Etidron has the lowest inhibition efficiency. This is due to it's the lowest molecular size (250) and lowest number of adsorption centres 9 centers (7-O, 2-P atoms).

CONCLUSIONS

- The investigated pharmaceutical compounds inhibit the corrosion of carbon steel in 0.5M HCl.
- The inhibition is due to adsorption of the inhibitors molecules on the carbon steel surface and blocking its active sites
- Results obtained from weight loss, dc polarization, ac impedance, EFM and surface examination using SEM–EDX techniques are in good agreement and show increased inhibitor efficiency with increasing inhibitor concentration.
- Adsorption of the inhibitor fits a Langmuir isotherm model.
- Polarization data shows that the investigated pharmaceutical compounds act as mixed-type inhibitor in 0.5 M HCl
- The theoretical study of inhibitors shows that the inhibition efficiency increases with increasing the energy of the highest occupied molecular orbital (E_{HOMO}), which means that the inhibitor acts as an electron donor when blocking the corrosion reaction sites.

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