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A Study into the Corrosion Inhibition of Carbon Steel in Acidic Medium Using Eco-Friendly Compounds

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Abstract

The corrosion inhibition effects of cefixima and aminobenzylpenicillin drug inhibitors in 0.05M deaerated sulfuric acid solution for carbon steel have been studied by using electrochemical techniques and quantum chemical calculations as well as scanning electron microscope (SEM). It is observed from the experimental findings that both compounds perform as good inhibitors and behave according to mixed type inhibitor in terms of their inhibitory action. Additionally, it was found the percentage of corrosion inhibition become maximal when the concentrations of the cefixima and aminobenzylpenicillin inhibitors are increased. The influence of temperature on the corrosion of carbon steel has been investigated and the activation energy values estimated. The corrosion efficiency decreases with increasing the temperature range. The parameters of thermodynamic have been determined and indicate that the adsorption mechanism follows the Langmuir isotherm model and forms a protective layer on carbon steel surface electrode, which was characterized by scanning electron microscope measurements, to prevent a corrosion process. Quantum chemical calculations have been performed to provide evidence for corrosion inhibition according to the chemical structures of the cefixima and aminobenzylpenicillin drug inhibitors.

Keywords: cefixima , aminobenzylpenicillin drug , corrosion inhibition, PM6, EIS measurements,

1. INTRODUCTION

Carbon steel is a metal that commonly used in the form of its iron alloys [1], in many industrial applications such as chemical processing, and oil production and refining [2],although it is comparatively expensive.

Furthermore, these applications typically have a serious impact on the metallic equipment *e.g.* pipelines, which are corroded by exposure to the aggressive acidic or alkaline media that are used in industrial processes [3]. Studies of carbon steel corrosion in acidic solutions is more common because of the importance of its application in several industrial operations such as pickling, cleaning, descaling, and petrochemical acid processes [4,5]. For instance, sulfuric acid and hydrochloric acids are commonly used in the pickling of carbon steel [6]. There are several methods to prevent and retard the corrosion process, which damages the metal, and amongst these methods one of the most common is the use of inhibitors. These are compounds that are added to aggressive environments to overcome the dissolution of the metal and its alloys into free ions and thus preserve the metals for a longer time[7].The most common and important inhibitors are organic compounds which contain heteroatoms, for instance oxygen, sulfur, *etc.* as well as aromatic rings which have enough electron density to share with empty orbitals on the metal [8]. Organic heterocyclic compounds containing S and N atoms are the most effective to decrease the corrosion processes and retard the anodic and / or cathodic reactions and are therefore classified as good corrosion inhibitors [9].Unfortunately, although these organic inhibitors are highly effective towards their influence on the half-reactions, and comparable with the inorganic compounds such as nitrite and chromate, *etc.* which may also be used as inhibitors. On the other hand, the latter are very dangerous with negative effects towards environmental pollution and are known to be not 'eco-friendly' [10]. The development of new inhibitors from natural sources is both important and desirable. There are similarities to the drug discovery process, as many chemical compounds which are used as medicines may be perfect applicants to substitute as conventional toxic compounds as inhibitors [11,12].The importance of the use of many drugs has led to the growth of corrosion inhibitors [7,13]. There are many previous reports which have examined drugs such as melatonin [7], valorization [13], antihypertensive [14],Ibuprofen salicylate [15], benzyl penicillin [16],amlodipine besylate[17],streptomycin [18], ketosulfone[19], pheniramine[20], imidazole-based antifungal [21], rhodanine azosulpha[22], cefalexin[23], and ceftriaxone[24], as corrosion inhibitors for iron and its alloys in several kind of acidic solutions. The present work involves investigation of cefixima and aminobenzylpenicillin corrosion inhibitors in 0.05M deaerated sulfuric acid solution for carbon steel by using the electrochemical methods as(OCP),(PDP) and (EIS) as well as quantum chemical calculations.The are coupled with scanning electron microscope to examine the characteristics of the electrode's surface in order to study the corrosion efficiency, corrosion rate, and the effect of temperature on the corrosion process.

2. EXPERIMENTAL

2.1. Electrochemical methods

Carbon steel was used as a working electrode in an electrochemical cell to investigate the inhibitory effects of corrosion on the steel when exposed to adeaerated 0.05M H_2SO_4acidic solution over a temperature range (303.15-318.15) K both in the absence and the presence of cefixima and aminobenzylpenicillin. The chemical composition of carbon steel has the following composition (wt.%) C (0.01), Si (0.06), Mn (0.40), Cr (0.04), Ni (0.05), Mo (0.03), Al (0.01), Cu (0.03), Nb (0.05),Ti (0.01), V(0.01), W(0.05), Pb (0.02), Zr (0.01), Co (0.06) and the remaining Fe. Specimens of the working electrode were prepared from the carbon steel before any measurement tests, the samples were polished using emery paper at different sizes, and used an aqueous alumina to obtain a mirror-like surface. Thus, the specimens were cleaned by using by hot benzene, acetone, distilled water and dried by passing nitrogen over the surface. The cross-sectional area that was exposed to the test solution was $1cm^2$.All experiments were carried at constant temperature by using a regulated circulating bath (HYSC company, Korea). A corrosion cell was constructed with carbon steel as the working electrode, a platinum electrode ($0.23cm^2$exposed surface for reaction) as a counter electrode and a Hg | $Hg_2Cl_{2(s)}$ | KCl) as the reference electrode (saturated Calomel electrode). The electrodes were placed in the corrosion cell and the contents measured by a Potentiostat/Galvanostat (GAMRY company, USA) to determine the OCP values and obtain the Tafel polarization curves. Data were analyzed by an Echem Analyst (version 6.33) to get the parameters of the electrochemical corrosion process at a polarized carbon steel electrode. The measurements of EIS were achieved at a frequency range from 0.2 Hz to 1000 Hz.

2.2. Corrosion inhibitors

A test solution was freshly prepared with distilled water in sulfuric acid(analytical reagent grade 97% which obtained from Scharlau company).Thus, to study the inhibitive action of cefixima and aminobenzylpenicillin drugs towards carbon steel, an 0.05M H_2SO_4dearated acidic solution was prepared at various concentrations (0.5-10) mM over a temperature range(303.15 - 318.15) K. Fig. 1 shows the chemical structure of the drugs compounds that were studied as corrosion inhibitors.

2.3. Characterisation of the surface electrode

The carbon steel samples were characterized with supporting data from scanning electron microscopy (ZEISS Sigma 300 type microscope at an accelerating voltage 15 kV). The test samples of $1cm^2$ exposed in test solution which immersed in 200 ml of 0.05M H_2SO_4dearated acidic solution with and

without of 10 mM drugs corrosion inhibitors for 10 h at 303.15 ± 1 K. The images were used to study the morphologies of the surface electrode specimens, and after each analysis these werewashed with distilled water and dried in preparation.

2.4. Theoretical calculations

The quantum chemical calculations were implemented by VAMP version 10.0 in Materials studio v8.0 package software from Accelrys Inc. The full geometrical optimization for ground state of cefixima and aminobenzylpenicillin drug inhibitors has been performed by employing the parametric method (PM6) [25,26] because this routine is highly dependable for estimating the electronic properties of molecules which have bulk numbers of orbitals and electrons. Its many modifications form other semi-empirical approximations allowed for seventy elements [25] to be parameterized, such as core-core interactions and the more accurate results involved the d-orbitals for the main group elements. The quantum chemical parameters were calculated for optimized structures of the drug inhibitors *e.g.*(LUMO) and (HOMO) values for the energy levels as well as molecular surface area, binding energy, and Mullikan atomic charges. Additionally, it is important to predict the energy gap (ΔE) value and traction of electron transferred (ΔN) which dependent on the Koopman's theory application [27,28].

3. RESULTS AND DISCUSSION

3.1. Open Circuit Potential

Usually the OCP depicts the complex phenomena that are related with the discharge potential relaxation within the electrical double layer to the electrode and/or with the semi-intensive "pseudo-capacitor" effect of chemical adsorption electro active intermediates on the working electrode surface [29]. Consequently, the measuring of open circuit potential for the working electrode over an interval of time is important to define a complete or partial inhibition and determine the threshold concentration of corrosion inhibition[30]. Fig.1 exhibits the variation in the OCP in the absence and the presence of cefixima and aminobenzylpenicillin drugs in 0.05M H_2SO_4 deaerated acidic solution at 30315K. In the absence of the drug inhibitors, the open circuit potential altered towards negative values. This behaviour reflects the dissociation of free metal initial process before the immersion of the thin oxide film that formed in air and later deposited on the metal [31]. In the presence of cefixima and aminobenzylpenicillin drugs, the OCP values (Table 1) drift slightly to positive direction as a result of the formation of the protective film on the surface of the carbon steel electrode [32]. Thus, in all inhibited cases, at first the OCP values increase to more noble values and

later reach a steady state rate with time (at this state the oxidation current is equal to the reduction current and reaches a state of equilibrium [33]). Meanwhile, the exact ranking of a chemical compound as either an anodic or cathodic inhibitor involves the displacement of the OCP values by more than 85mV[2]according to the OCP value in the nonappearance of inhibitors. Therefore, the displacement of OCP valueswhich does not exceed ~ 20 mV in the presence of inhibitors. This value is not enough to take the decision to classify it as an anodic or cathodic inhibitor. In other words, the cefixima and aminobenzylpenicillininhibitors act as a mixed-kind inhibitors.

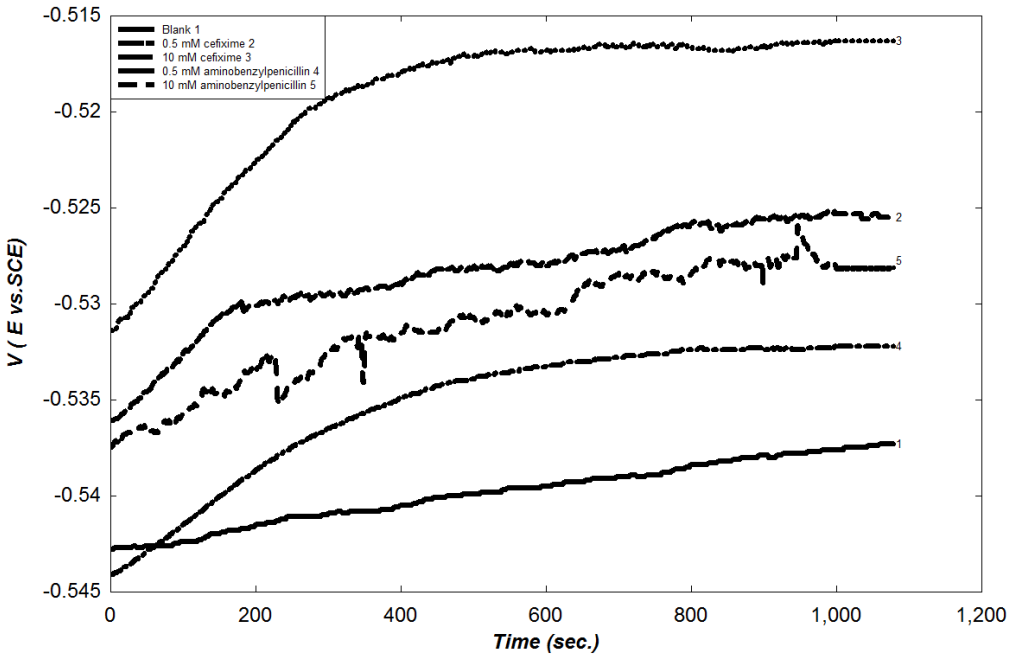

Fig (1) : The OCP curves for carbon steel at(0.5 and 10 mM concentrations) of cefixima and aminobenzylpenicillin drug inhibitors,under the experimental conditions

3.2. Potentiodynamic Polarization Curve measurements

The potentiodynamic polarization measurements have been performed to gain knowledge which relates to the corrosion kinetics that are associated with the cathodic and anodic reactions. The measurements of potentiodynamic polarization have been carried out at a scan rate ±2.0 mV at the potential range ±150 mV.Fig. 2to demonstrate that the overall kinetics of anodic and cathodic reactions that happen on the carbon steel electrode of cefixima and aminobenzylpenicillin drug inhibitors in0.05M H_2SO_4deaerated acidic solution at 303.15 K. The arithmetical values for the variation of the corrosion potential ($E_{corr.}$), the corrosion current density ($i_{corr.}$), cathodic and anodic Tafel slopes (β_c , β_a), correspondingly as well as the surface coverage

degree (θ) and the percentage of inhibition efficiency ($\eta_p\%$) have been collected in Table 1. These data were obtained by fitting a method to Tafel lines for "Stern-Geary equation" The values of surface coverage degree and corrosion inhibition efficiency [30,31] have been calculated from equations (1) and (2),respectively as shown in below.

$$\theta = \frac{i_{\text{corr.uninhibited}} - i_{\text{corr.inhibited}}}{i_{\text{corr.uninhibited}}} \text{ ....(1)}$$

$$\eta_p\% = \theta \times 100 \text{ .....(2)}$$

The values of ($i_{\text{corr.uninhibited}}$)and ($i_{\text{corr.inhibited}}$)referred to the corrosion current densities in without and with cefixima and aminobenzylpenicillin inhibitors, respectively.

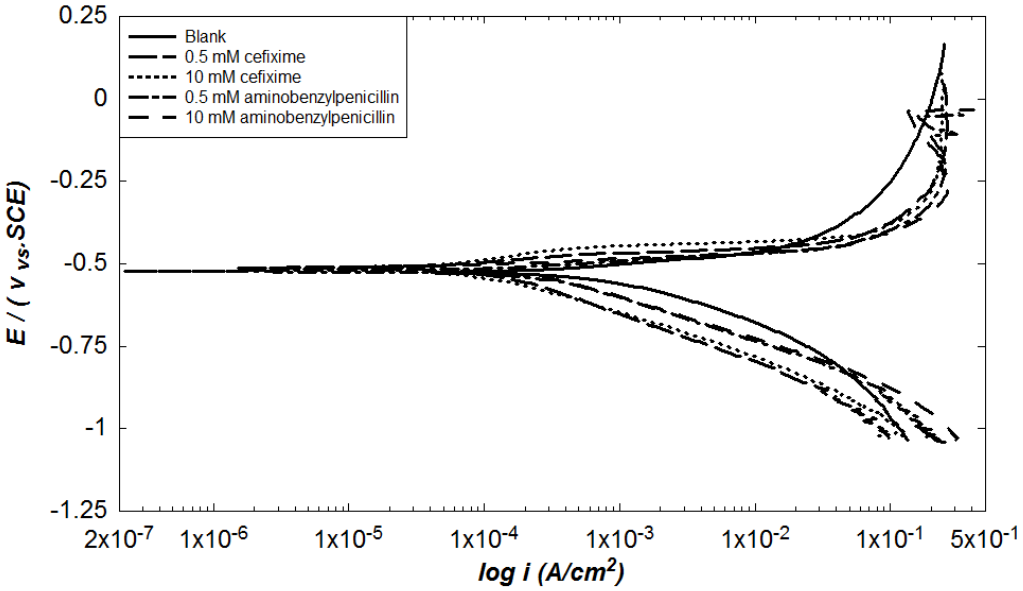

Fig (2) : Tafel polarization curves for carbon steel at(0.5 and 10 mM concentrations) of cefixima and aminobenzylpenicillin drug inhibitors ,under the experimental conditions.

Table (1): Kinetic parameters of corrosion, percentage inhibition efficiencies and coverage degree for carbon steel in various concentrations of cefixima and aminobenzylpenicillin drug inhibitors in 0.05M H_2SO_4 dearated acidic solution at 303.15K

Concentration (mM)	$i_{corr.}$ (A/cm²)	- E_{OCP} (mV	- E_{corr} mV)	β_a(mV/ decade)	β_c (mV/decade)	Corrosion Rate (mpy)	θ	$\eta\%$
Blank	1.15×10^{-3}	0.534	526.0	116.7	170.5	524.3	-	-
Cefixime								
0.5	4.26×10^{-4}	0.527	508.0	83.80	146.6	194.7	0.6295	62.95
1.0	2.96×10^{-4}	0.525	514.0	79.40	135.0	135.3	0.7426	74.26
3.0	1.19×10^{-4}	0.527	512.0	69.10	151.1	54.31	0.8965	89.65
6.0	6.39×10^{-5}	0.516	514.0	65.10	116.4	29.18	0.9444	94.44
10	4.49×10^{-5}	0.520	501.0	60.50	118.7	20.51	0.9609	96.09
Ampicillin								
0.5	2.42×10^{-4}	0.541	523.0	72.90	130.7	110.4	0.7895	78.95
1.0	2.41×10^{-4}	0.532	512.0	70.30	134.8	110.1	0.7904	79.04
3.0	2.17×10^{-4}	0.534	507.0	83.10	185.5	99.20	0.8113	81.13
6.0	8.90×10^{-5}	0.522	500.0	43.00	164.1	40.66	0.9226	92.26
10	1.28×10^{-5}	0.528	502.0	39.10	84.90	5.843	0.9888	98.88

It is clear from the (Table 1), that the ($i_{\text{corr.inhibited}}$) and corrosion rate values decrease with increasing the concentration of cefixima and aminobenzylpenicillin inhibitors. The observations are consistent with increasing values of coverage surface degree and corrosion inhibition efficiency. As predicted, the addition of corrosion inhibitors to the 0.05 M sulfuric acid reduced the dissolution of free metal in anodic reaction and the cathodic reaction by retarding the hydrogen evolution reaction. This occurs consequently of the adsorption of the drug inhibitors on thecarbon steel electrode which in turn block the active site [36]. The inhibitory action may affect either or both theanodic and cathodic corrosion reactions [37]. As shown from Table 1, Fig. 2 The cathodic and anodic Tafel slopes have been changed with increasing the corrosion drug inhibitors, indicating that the inhibitors

exert control on the half-reactions of the corrosion process. It is a clear demonstration that the Tafel lines are parallel and similar as shown in Fig.2, which was obtained from the different drug inhibitors. When the concentration of cefixima and aminobenzylpenicillin inhibitors are increased this leads to a reduction in the anodic and cathodic currents and, slightly remarkably, in cathodic drift in the corrosion potential values. Generally, the potential-current curves that are recoded with the drug inhibitors are described by the attendance of breakdown anodic potential [38]. This behaviour confirmed the noble shift in corrosion potential values with decreasing the ($i_{\mathrm{corr.inhibited}}$)in the presence of cefixima and aminobenzylpenicillin inhibitors. This reflects to form a protective film on the surface of the carbon steel electrode. Thus, according to decrease in corrosion current densities by introducing the inhibitors in aggressive sulfuric acid solution could be considered the inhibition action of cefixima and aminobenzylpenicillin inhibitors based on the mixed-type inhibitor.

3.3 Electrochemical impedance spectroscopy measurements

The effect of inhibitor concentration on behaviour of electrochemical impedance of carbon steel in 0.05 M deaerated sulfuric acid solution has been studied and compared with the results of polarization experiments using Tafel measurements. Thus, the Nyquist plots obtained with representative Bode diagrams for the cefixima and aminobenzylpenicillin inhibitors in (0.5 and 10 mM concentration) at 303.15 K are shown in Fig. 3 and Fig. 4 a and b, respectively. It is clear Nyquist plots describe semi-circular shapes as well as one time constant, which are displayed in the Bode diagram. This refers to the corrosion of carbon steel in deaerated acidic solution is primarily controlled through the process of charge transfer [35,36]. Even though the Nyquist plots remain without change in general style, the diameter of the semi-circular portion of the plot increased following the addition of the corrosion inhibitors in the aggressive media and the resulting enhanced corrosion resistance of the carbon steel electrode. This increase is more pronounced with increasing drug inhibitor concentration, which is consistent with the adsorption process of cefixima and aminobenzylpenicillin drugs molecules on the surface electrode. There is a general depression in the Nyquist plots *i.e.*, there are not a perfect semi-circular form as predicted from the principles of electrochemical impedance spectroscopy. This deviation from the ideal vision occurs as a result of the dispersion in frequency and is obtained from the roughness and heterogeneous electrode surface besides adsorbed the cefixima and aminobenzylpenicillin inhibitor molecules on the carbon steel working electrode [37,38]. Fig. 3 and Fig. 4a,b assume that a similar mechanism happens for the corrosion of carbon steel with the drug

inhibitors and does not have an effect on the shape of the impedance diagram [30]. However, in the terminal curves for the Nyquist plots appear to display a clear and long capacitive loop a thigh concentrations of the drug inhibitors. This is believed to be associated with several main factors, such as the behaviour of a double layer and the charge transfer process, and is credited with the relaxation process due to the adsorption of inhibitor drug molecules and iron sulfate species [1,39] on the surface of the electrode as shown in the following figures, " Fig.3 and Fig. 4a,b."

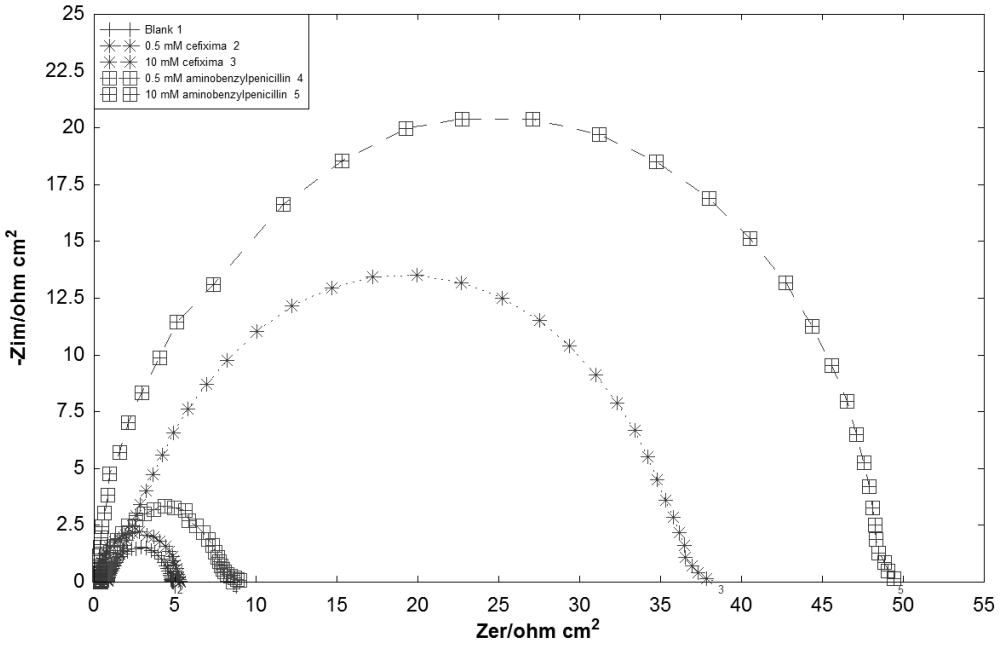

Fig (3) : Nyquist plots for the cefixima and aminobenzylpenicillin drug inhibitors at (0.5 and 10 mM concentrations) at 303.15.

Table (2): Impedance information forcarbon steel in various concentrations of cefixima and aminobenzylpenicillin drug inhibitors in 0.05M H_2SO_4 dearated acidic solution at 303.15K

Concentration, mM	Rs×10^{-3} (Ω cm^2)	Rct (Ω cm^2)	CPE ×10^6 (Ω^{-1} cm^{-2})	n	Cdl ×10^4 (μF cm^{-2})	$\eta\%$
Blank	302	1.925	498.8	0.992	4.7462	-
Cefixime						
0.5	784	4.080	999.8	0.840	3.5194	52.81
1	756	7.396	801.8	0.806	2.3392	73.97
3	559	8.295	531.8	0.838	1.8724	76.79
6	526	15.44	212.8	0.887	1.0285	87.53
10	838	32.08	112.8	0.889	0.5559	93.99
Ampicillin						
0.5	470	7.851	719.4	0.904	4.1649	75.48
1	412	9.11	610.4	0.888	3.1878	78.86
3	583	10.14	301.7	0.917	1.7950	81.01
6	385	22.88	164.2	0.988	1.5352	91.58
10	181	23.67	125.8	1.000	1.2580	91.86

The electrochemical impedance spectroscopy parameters that were obtained were fitted to a suitable equivalent circuit diagram shown in Fig. 5, depending on the general shape of Nyquist plot to model the interface interaction between the drug inhibitors and the carbon steel working electrode in deaerated 0.05M H_2SO_4 acid solution and the results are illustrated in Table 2.

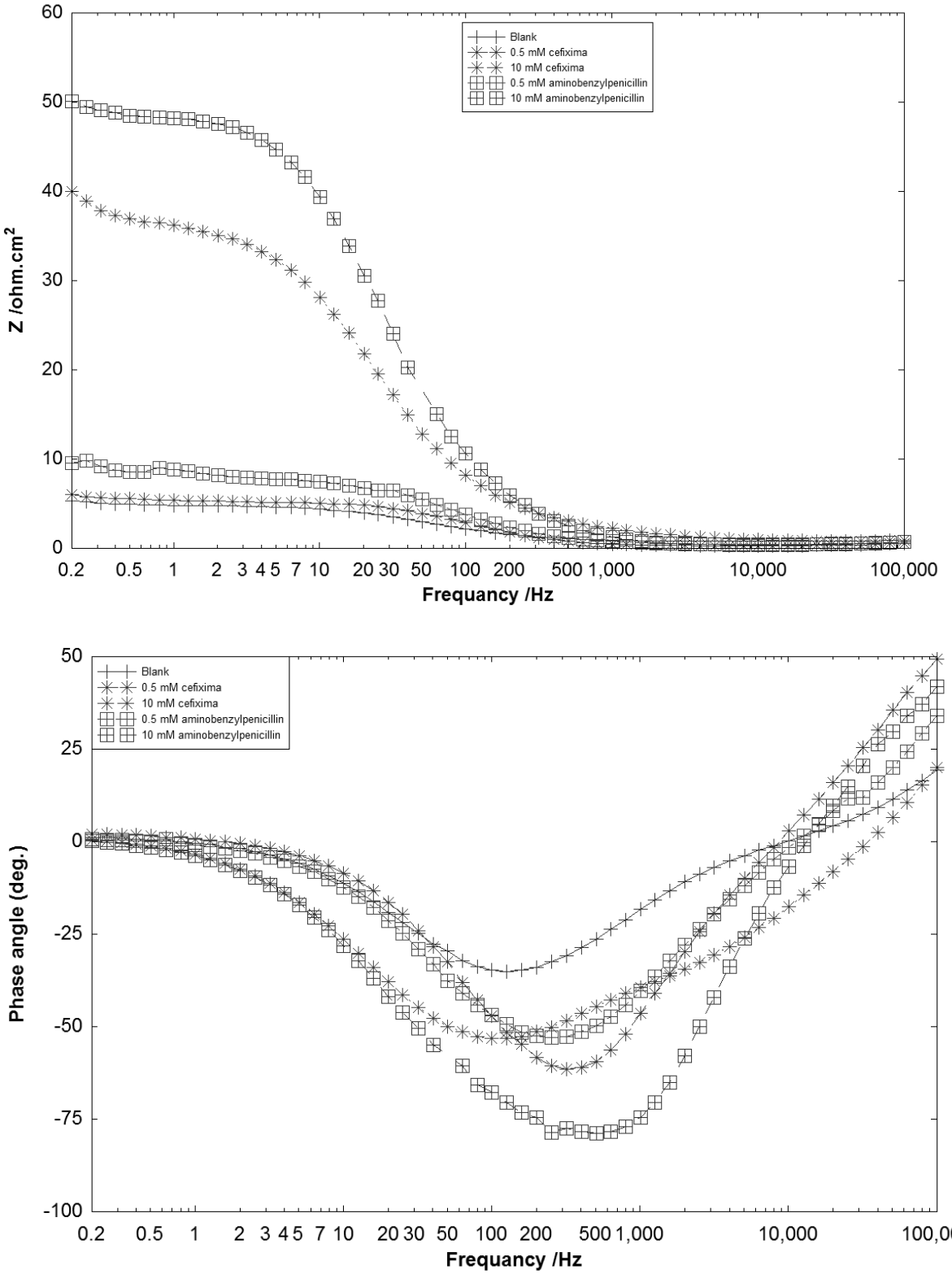

Fig. (4) : Bode plots (Bode model **a** and Bode phase **b**) for the corrosion of carbon steel with and without drug inhibitors at 303.15 K.

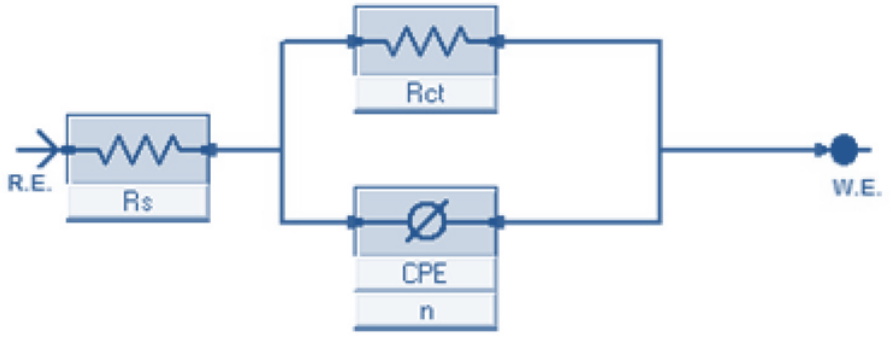

Fig. (5) : The suitable equivalent circuit diagram for the EIS measurements

The equivalent circuit diagram that is used consists of the R_s, R_t, and CPE are "resistance of solution", "resistance of charge transfer" and "constant phase element" respectively. Thus, the CPE represents the capacitance of electrical double layer "Cdl" that explains the behaviour of the whole heterogeneous system and to yield more accuracy when applied to the experimental results[44]. The circuit diagram placed R_t in parallel to the CPE which is defined by Y_0 which is the coefficient of CPE and n is an exponent or could be defined as the phase shift to give a picture of the degree of inhomogeneity of the surface [45]. The equation $Z_{CPE} = Y_0(i\omega)^{-n}$ is used to calculate the CPE, the symbols i and ω are the angular frequency and imaginary number, respectively. As mentioned in a published report [41], the CPE behaves as ideal capacitor if the value of n is equal to unity. The value is corrected for the real or true capacitance after calculation from the following equation [46]

$$C_{dl} = \frac{1}{2\pi f_{max} R_t} \ldots\ldots\ldots\ldots (3)$$

f_{max} is the "frequency at which the imaginary part of the impedance reaches a maximum". It is clear from Table 2 when adding the drug inhibitors to an aggressive medium, the resistance values of charge transfer are increased and consistent with the reduction of the electrical double layer capacitance; it seems more noticeable as the drug inhibitors concentration is increased. The numerical values of C_{dl} decrease as a result of the reduction in thickness of electrical double layer and/or a decrease in the dielectric constant [47]. This, in turn, leads to adsorption of cefixima and aminobenzylpenicillin inhibitor molecules on working electrode surface *via* the interface boundary between the metal and electrolyte and the imperceptible replacement of H_2O molecules by cefixima and aminobenzylpenicillin molecules and reduces the extent of metal dissolution. This indicates that the surface of carbon steel is protected from attack of the acidic media and furthermore the variation of $n$parameters which enhances the understanding of drug inhibitors and the concept of heterogeneity of the carbon steel surface electrode [48]. Consequently, the

inhibition efficiency percentage is calculated according to equation 4[49] as collected in Table 2. The efficiency of corrosion inhibition is increased with the increase in the concentration of inhibitors used. This offers the charge transfer resistance is chiefly controlling the corrosion of the working electrode.

$$\eta_p\% = \frac{R_{ct,inhibitied} - R_{ct,uninhibitied}}{R_{ct,inhibitied}} \times 100 \ldots\ldots\ldots\ldots(4)$$

The symbol of $R_{ct,inhibitied}$ is the "charge transfer resistance" with various concentrations of drug inhibitors and $R_{ct,uninhibitied}$ the "charge transfer resistance" in the absence of inhibitors. Values of $\eta_p\%$ differ slightly from those estimated from potentiodynamic measurements, due essentially to the factors which are associated with the above technique in spite of the same general trend. Likewise, the Bode plots are shown in Fig. 4a and Fig. 4b for the corrosion of carbon steel with and without drug inhibitors in 0.05 M deaerated sulfuric acid solution at 303.15 ± 1 K; it is noticeable from the diagrams, that the Bode phases are dissimilar with different values . Despite the similarity in the general style of the Nyquist plots, the phase angle increases at high concentrations of cefixima and aminobenzylpenicillin inhibitors to reach the optimal level. A clear peak appears at the higher frequencies when the drug inhibitors are added which enhance the condensation of the protective layers of inhibitors on the working surface. This is accompanied by the adsorption of the cefixima and aminobenzylpenicillin inhibitors and reduce the dissolution rate of metal [50]. Furthermore, the slopes of the lines of the Bode plots are not equal to unity and this deviation reflects the heterogeneity of the surface of the electrode [51].

3. 4Effect of temperature and adsorption considerations

The influence of temperature parameter on the corrosion of working electrode(carbon steel) in the absence and in the presence of cefixima and aminobenzylpenicillin inhibitors (each 10 mM) was examined in deaerated 0.05 M sulfuric acid solution. Measurements were made over a range of temperatures (303.15 - 318.15) K by employing the potentiodynamic method. Consequently, the corrosion current density that had been estimated from the Tafel plot analysis was used to assess the activation energy value (E_a),, which gives a clear vision about the mechanism for the adsorption process. The basis for this analysis is the Arrhenius equation (Eq. 5)[35], which relates the corrosion rate and the degree of temperature:

$$i_{corr.} = A - \left(\frac{-E_a}{RT}\right) \ldots\ldots 5$$

The symbols "*A*, E_a , *R* and *T*" are the "pre-exponential factor", "activation energy", "gas constant" and the "temperature" values, respectively. Results are given in Tables3, from which it is observed that the corrosion rate and corrosion current density increase by means of the temperature increases and this reflects the reduction in the corrosion efficiency, due to the desorption [39] of drug inhibitors from surface of the carbon steel electrode. The activation energy values observed are higher when the drug inhibitors are present (Table 4 and Fig. 6). This behaviour is often indicative that the physisorption process of drug inhibitor moleculesis taking place on the carbon steel surface electrode and leads to the formation of an adsorptive layer which has electrostatic properties [52]. However, this can only be used as a guide: it is not considered conclusive because of the water molecules on the electrode surface, which participate in a competitive adsorption process, while to remove them from the carbon steel surface electrode requires a significant activation energy [31,49]. This means that both the physisorption and chemisorption processes happen instantaneously [54] enabling the drug speciesto be adsorbed on the metal surface.

Table (3): Kinetic parameters of corrosion, percentage inhibition efficiencies for carbon steel at optimum concentration (10 mM)cefixima and aminobenzylpenicillin drug inhibitors in 0.05M H_2SO_4 dearated acidic solution in temperature range from 303.15K to 318.15K.

Temperature (K)	$i_{corr.}$ (A/cm²)	- E_{corr} (mV)	β_a(mV/decade)	β_c (mV/decade)	Corrosion Rate (mpy)	$\eta\%$
Blank						
303.15	1.15×10^{-3}	526.0	116.7	170.5	524.3	-
308.15	3.36×10^{-3}	501.0	96.30	136.1	1.537×10^3	-
313.15	1.42×10^{-2}	493.0	128.4	197.7	6.487×10^3	-
318.15	2.57×10^{-2}	487.0	167.8	255.6	11.73×10^3	-
Cefixime						
303.15	4.49×10^{-5}	501.0	60.50	118.7	20.51	96.09
308.15	4.36×10^{-4}	479.0	84.80	170.2e	199.3	87.02
313.15	2.22×10^{-3}	479.0	113.7	183.8	1.016×10^3	84.36
318.15	4.53×10^{-3}	481.0	124.4	198.6	1.613×10^3	82.37
Ampicillin						
303.15	1.28×10^{-5}	502.0	39.10	84.90	5.843	98.88
308.15	4.74×10^{-5}	485.0	71.80	71.80	21.66	98.58
313.15	4.34×10^{-4}	487.0	77.10	157.4	198.3	96.94
318.15	9.35×10^{-4}	487.0	93.40	146.9	198.7	96.36

Table (4) : Kinetic and thermodynamic parameters for carbon steel of cefixima and aminobenzylpenicillin drug inhibitors in 0.05M H_2SO_4 deaerated acidic solution in temperature range from 303.15K to 318.15K.

Kinetic parameters			Thermodynamic parameters			
Conc. inh. (mM)	E_a (kJ/mol)	r^2	slope	$K_{adsorp.}$ M^{-1}	$-\Delta G_{adsorp.}$ kJ/mol	r^2
Blank	172.833	0.9901				
Cefixime	248.9028	0.9784	1.00	3196.9594	30.4677	0.9999
Ampicillin	242.2452	0.9859	0.99	2688.3064	30.0309	0.9979

On the basis of these indicators, it is possible to determine the relationship between the surface of the electrode and the corrosion inhibition so as to elucidate the type and strength of adsorption process. Therefore, the potentiodynamic test data, which relate the degree of surface coverage with concentration at different temperatures, are fitted by using Langmuir's adsorption isotherm to yield the best correlation regression value r^2 (Table 4 and Fig. 7).

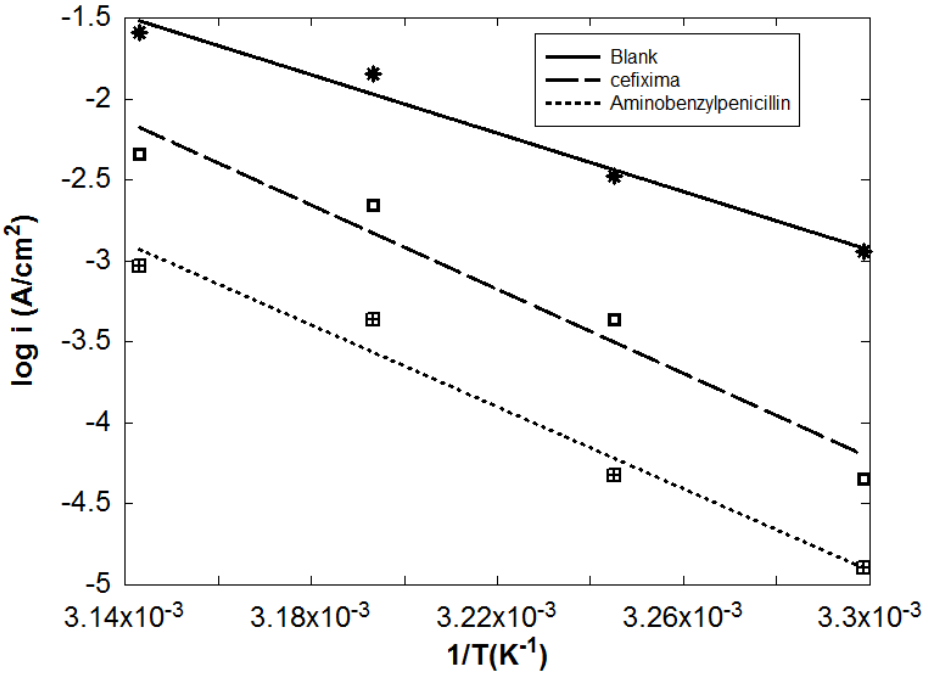

Fig (6) : Arrhenius plots of log i (A/cm^2) versus 1/T (K^{-1}) at various concentrations of drug inhibitors.

The Langmuir adsorption equation, which describes the monolayer of protective film that forms on the electrode surface is expressed by the following equation [31,51–55].

$$\frac{C_{corr.inhib.}}{\theta} = \frac{1}{K_{adsorp.}} + C_{corr.inhib.} \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

The symbols $C_{corr.inhib.}$, θ and $K_{adsorp.}$ refer to the concentration of drug inhibitors, the surface coverage degree, and the equilibrium constant which relates the adsorption and desorption processes and is utilized to estimate the free energy ($\Delta G^0_{adsorp.}$) of inhibitor adsorption according to the following equation

$$\Delta G^0_{adsorp.} = -2.303\ RT\ log_{10}(55.5\ K_{adsorp.}) \quad \ldots\ldots\ldots\ldots(7)$$

The numerical value "55.5"refers to the concentration of water that is uttered in units of $\frac{mol}{dm^3}$. It is clear from Table 4 and Fig. 7 that the values of r^2 and slopes are approaching unity which follows the Langmuir's adsorption isotherm . Thus, as the values of $K_{adsorp.}$ obtained with the cefixima and aminobenzylpenicillin inhibitors are higher, this is an indication of the feasibility of adsorption of species drugs on the electrode surface, rather than desorption [59]. Moreover, the values of $\Delta G^0_{adsorp.}$negative that got for both cefixima and aminobenzylpenicillin in inhibitors reflect the spontaneous nature of the adsorption and the constancy of the protective layer that forms on

working surface [55,54]. Normally, a value of standard free energy up to " -20 kJ mol^{-1} " or less corresponds with the electrostatic interactions that exist between the charged surface electrode and the inhibitor species following the physisorption process. however, when the value of $\Delta G^0_{adsorp.}$ is close to "-40 kJ mol^{-1}" or more indicate to share and transfer of electron density between metal surface and the inhibitor molecules and formed the coordinate bond between them (define as chemical adsorption) [60–63]. Accordingly, the $\Delta G^0_{adsorp.}$ values of both drug inhibitors are less than -40 kJ mol^{-1} , refers to the physisorption process occurred with electrostatic interactions and associated with other interactions may take place to enhance the adsorb protecting film on the surface electrode *via* chemical adsorption process. Consequently, the cefixima and aminobenzylpenicillin inhibitors adsorbed on the carbon steel surface electrode in acidic solution through the physical and chemical adsorption types and predominantly with the chemical character[50,60,61].

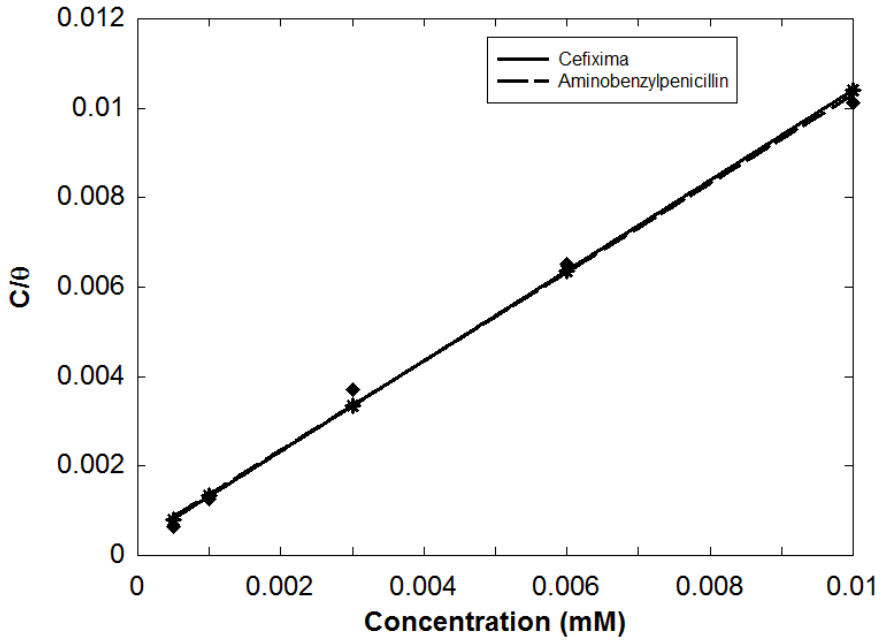

Fig (7) : Langmuir adsorption isotherm of drug inhibitors on the carbon steel at different temperatures.

3.4. Scanning electron microscopy analysis

A series of images were obtained as part of a scanning electron microscopy (SEM) investigation to illustrate the differences in the morphology of the surface of an carbon steel working electrode following exposure. Thus, the SEM images show the surface before exposure (Fig. 8a), and following 3 hours immersion in (0.05 M) sulfuric acid solution in the presence of 10 mM of each inhibitor: cefixima (Fig. 8b) and aminobenzylpenicillin (Fig 8c). It is clear from Fig.8a, that the facets of carbon steel surface suffer damage, due

to the corrosive action of the acidic, as well as displaying cracks and deep pits leaving the surface appearance very rough with crevices. Furthermore, the colour of surface tend to be grey-black, due to the characteristic colour of the Fe_3C film[66–68]. Following the addition of both the cefixima and aminobenzylpenicillin inhibitors, the surface electrode appears to be protected from the attack of acid (Fig. 8b and 8c) as few cracks and pits appear, and the previously rough surface morphology has become smooth consequently of the creation of a protective layer. As a result, the cefixima and aminobenzylpenicillin inhibitors retard the rate of corrosion and protect the carbon steel surface. Furthermore, a comparison of the images inFig.8b and Fig.8c, demonstrates clearly that the cefixima inhibitor provides protection more than the aminobenzylpenicillin in inhibitor and this is in agreement with the aforementioned results in this paper.

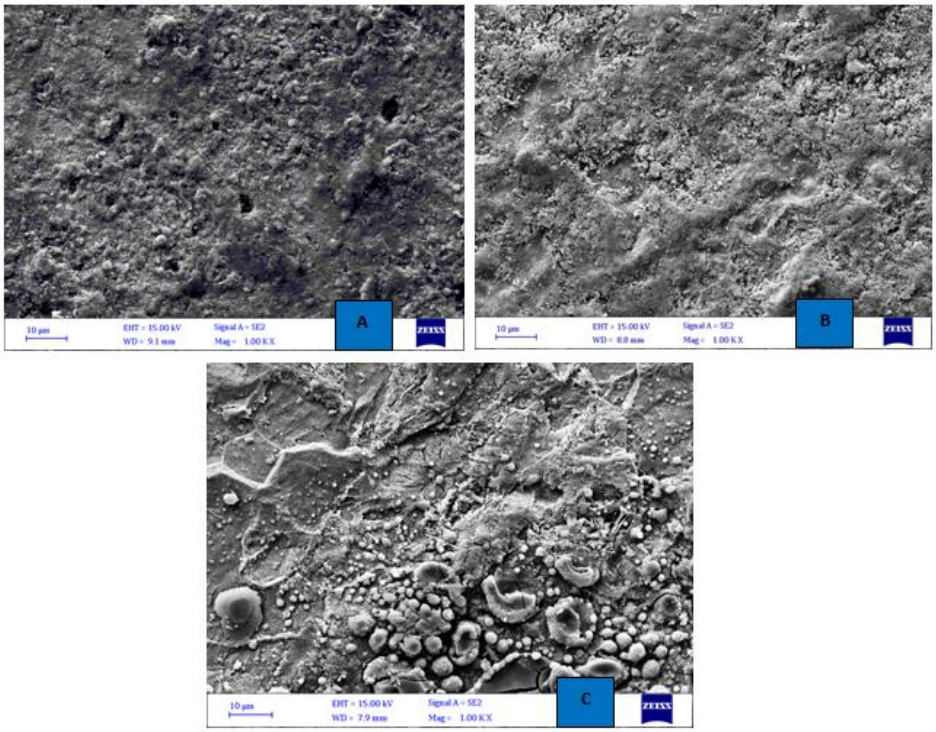

Fig (8): SEM images for the corrosion of carbon steel morphology in the absence (**a**) and in the presence of cefixima (**b**) and aminobenzylpenicillin (**c**) drug inhibitors at 303.15 K

3.5. Mechanism of corrosion inhibition

The idea for the adsorption process is a mostly a way to give an interpretation of the mechanism of corrosion inhibition for the organic compounds. More references mention the action of retarding the corrosion rate and preventing the metal surface from corrosion by aggressive

environments, some of these methods include decreasing the exposed surface area that may undergo reaction by blocking the active sites, or by adjusting the values of the activation energy when it is added into the medium [69]. On the basis that the change in open circuit potential values in the presence of drug inhibitors (as was noted in section 3.1) which specifies and evaluates the blocking effect on the surface of the carbon steel surface [70–72]. Moreover, the adsorption aspects allowed the values of $\Delta G^0_{adsorp.}$ to be elucidated for the cefixima and aminobenzylpenicillin inhibitors that are adsorbed on the working electrode surface through two types of simultaneous adsorption processes. The cefixima and aminobenzylpenicillin inhibitors may be adsorbed on the carbon steel surface through the unshared electron pairs on the heteroatoms such as nitrogen and sulfur or *via* the electron density for the double bonds and the π electrons of benzene ring for the aminobenzylpenicillin inhibitor. These species act as donors for the electron density towards the unoccupied d-orbital of the metal as acceptor and form co-ordinate covalent bonds [73]. Furthermore, the adsorption process occurs through the basis of the interactions between different charges *i.e.* by the "electrostatic interactions" between the inhibitor species and the metal surface and after that charge transfer occurs between these through the formation of a coordinate bond [74–76]. In particular, the accurate determination of the type of surface charge electrode is important to know which molecules adsorb first on its surface, especially when estimating the value of "Antropov's potential"[48].

However, from the OCP data and extrapolation the information for previous reports [41,77–79] suggest that the electrode surface has a positive charge. Therefore, it can be established that the cefixima and aminobenzylpenicillin inhibitors undergo protonation through the nitrogen atoms and have a net positive charge. According to this result, it is difficult for the rings to approach as they are similarly charged, leading to repulsion, so the protonated species of the drug inhibitors are adsorbed on the electrode's surface *via* the sulphate ions, which act as a bridge between the cation molecules and surface electrode [72,75–77], and later through the iron sulfate species $(\mathrm{FeSO_4^{2-}})_{\mathrm{adso.}}$, in the anodic reaction on the surface electrode according to the later steps of the corrosion mechanism in sulfuric acid solution [41]. The approach of the cationic species of the drug inhibitor [D.inh. molecules $\mathrm{H_x}]^{x+}$ is facilitated by the action of the electrostatic interactions allowing it to be adsorbed on carbon steel surface besides form a protective layer $[\mathrm{FeSO_4^{2-}}$D.inh. molecules $\mathrm{H_x}]^{x+}_{\mathrm{adso}}$. It is known that the cathodic reaction of the corrosion process involves hydrogen evolution, according to the following equation [41] $[\mathrm{FeH}]_{\mathrm{adso.}} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{Fe} + \mathrm{H_2}\uparrow$ ..... (8). This means that a competitive action between the hydrogen ions and cation drug molecules develops and

then adsorbs the protonated molecules on the cathodic active site, thus preventing liberation of hydrogen gas to retard the cathodic reaction. Additionally, may be participated that the unprotonated drug inhibitors participate in corrosion inhibition through chemisorption by the unoccupied electrons, and in other ways as discussed earlier. Fig. 9 illustrates steps mechanism of synergistic effect between the sulfate ions and the drug inhibitors on the electrode's surface. It is clear that the protonation step in the sulfuric acid solution involves (*x*) numbers of hydrogen ions that are in close proximity to the inhibitor molecules and the degree of protonation depends on the hydrogen ion scale (pH of solution), which increases with decrease in solution acidity [75,78].

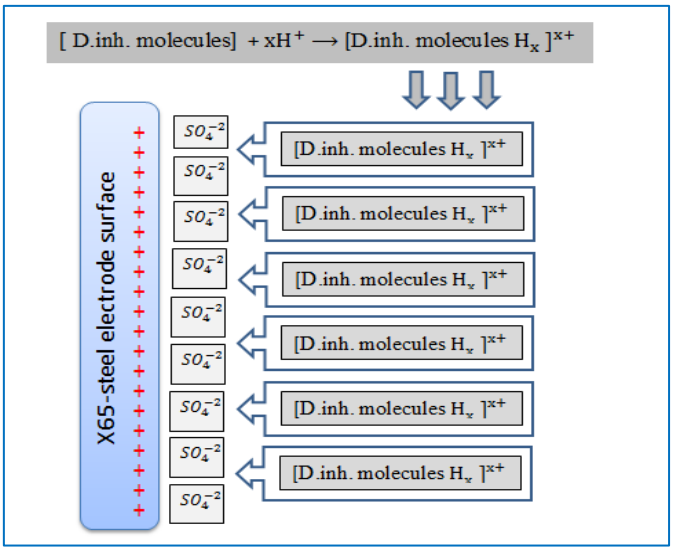

Fig. (9). Schematic illustration the mechanism of inhibition between sulphate ion and protonated drug inhibitor for the corrosion of carbon steel

3.5 computational treatment

The experimental results confirm the observation that aminobenzylpenicillin and cefixima act as good inhibitors to the carbon steel electrode in sulfuric acid solution. Moreover, the theoretical calculations can be used to estimate some of the electronic properties to verify the inhibitory action by comparing *e.g.* E_{HOMO}, E_{LUMO}, the "energy gap" between the (E_{LUMO}) and (E_{HOMO}) energies, the Mulliken atomic charges of hetro-atoms, "binding energy", and the molecular surface area of the optimized molecular structure using the semi-empirical PM6 method [84,85]. Table 5 shows the electronic parameters and optimized structures of aminobenzylpenicillin and cefixima inhibitors as illustrated in Fig.10a,b. It is observed the energies of (E_{HOMO}) (Fig 10) and (E_{LUMO}) (Fig 10) are related to the protection efficiency percentage: the higher the value of (E_{HOMO}) the greater the number of electrons that may be donated. This is consistent with the observation that molecules with molecular orbitals of lower energy levels show increased adsorption of

molecules, which promotes the corrosion inhibition. Similarly, the (E_{LUMO}) values refer to the aptitude of the molecule to accept electron density. In general, the gap in the energy values indicates kinetic stability and a large difference suggests high kinetic stability and low chemical reactivity, so when the energy gap of the frontier orbitals is lower then this leads to strong interaction of reactant species and optimum inhibition efficiency [86–91].

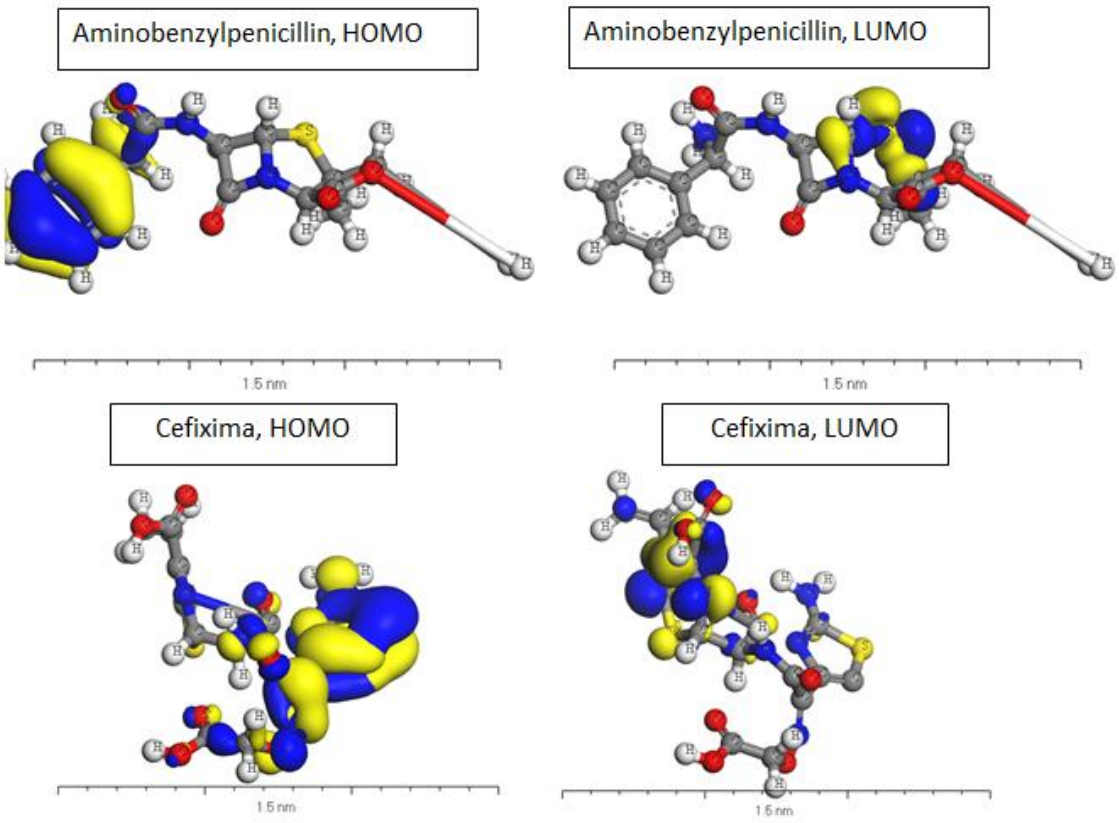

Fig (10) : HOMO and LUMO images for the cefixima and aminobenzylpenicillin drug inhibitors at PM6 calculations, respectively

It is clear that the values of the quantum chemical parameters confirm that the aminobenzylpenicillin inhibitor has slightly greater potential to act as a corrosion inhibitor than the cefixima inhibitor. These results are consistent with values of fraction electrons transferred from aminobenzylpenicillin and cefixima inhibitors to metal iron (ΔN) which were calculated according to equation (9)

$$\Delta N = \frac{\chi_{iron} - \chi_{inhibitor}}{2(\eta_{iron} - \eta_{inhibitor})} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Table (5) : Quantum chemical date for the cefixima and aminobenzylpenicillin drug inhibitors

Electronic properties	Cefixime point group (C1)		Ampicillin point group (C1)	
HOMO (eV)	-8.856		-9.691	
LUMO (eV)	-1.501		-0.905	
ΔE (eV)	7.355		8.786	
ΔN	0.247		0.193	
Binding energy ($kCalmol^{-1}$)	-124942.016		-94488.080	
Molecular surface area($Å^2$)	397.559		379.022	
Core-core repulsion (eV)	39065.989869		26969.672544	
Mulliken atomic charge	S_1	-0.087	S_1	-0.199
	S_2	0.067		
	O_3	-0.543	O_2	-0.434
	O_4	-0.438		
	O_5	-0.528	O_3	-0.420
	O_6	-0.521		
	O_7	-0.130	O_4	-0.448
	O_8	-0.566		
	O_9	-0.557	O_5	-0.526
	N_{10}	-0.420		
	N_{11}	-0.640	N_6	-0.496
	N_{12}	0.020		
	N_{13}	-0.495	N_7	-0.659
	N_{14}	-0.576	N_8	-0.643

The parameters which were used in the calculation are defined in detail in previous reports [92–97]. If $\Delta N < 3.6$ then this implies to increase the donation of electron transfer from the aminobenzylpenicillin and cefixima molecules to the surface of the metal [91,92] and corresponds with an increasing value of $\eta_p\%$, the results are shown in Table 4 and are in agreement with the experimental observations. Additionally, the Mulliken atomic distribution of hetero-atomic

molecules shown in Table 4 describe the possible active sites in the inhibitor molecule that bear a higher negative charge to participate in electrostatic attraction [95,98]. In other words, as mentioned in elsewhere [12,99] the values are very instructive and a good indicator to interpret the active site for the organic compounds when it interacts with a metal surface. The localization of the high negative charge on hetero-atoms in drug inhibitor molecules is related to the susceptibility towards adsorption on the surface of the electrode through the donor-acceptor reactions [37,89,100,101]. Furthermore, the values of binding energies were higher for the aminobenzylpenicillin and cefixima inhibitors which indicates the stability of the adsorbed aminobenzylpenicillin and cefixima molecules. This means that it is difficult to detach the species from the surface of the metal electrode easily and become a part of it. Thus, the molecular surface area values were calculated and the largest value calculated for the surface area is (397.559$Å^2$) for the cefixima inhibitor (Table 5), the difference in the geometry-optimized structures of the inhibitors enhances the effectiveness of coverage degree of the working electrode surface and leads to an increase in protection efficiency [102,103] as depicted in Fig.10a,b. It is clear the large value of the molecular surface area and the high negative binding energy for the cefixima inhibitor confirms that it displays the highest efficiency percentage of efficiency of corrosion inhibition.

3.6. Conclusions

The corrosion inhibition of carbon steel electrode in 0.05 M deaerated sulfuric acid solution by aminobenzylpenicillin and cefixima drug compounds were studied by electrochemical techniques, scanning electron microscope and the quantum chemical calculations. On the basis of experimental findings and theoretical estimates, the following observations can be made:

1. Aminobenzylpenicillin and cefixima drugs are excellent inhibitors for the carbon steel electrode in 0.05 M deaerated sulfuric acid solution and the inhibitory effectiveness of these compounds depends on the inhibitor concentration besides the inhibition efficiency percentage increased at high concentration of drug inhibitors
2. Both drug inhibitors act to retard the anodic and cathodic reactions and behave as mixed-type corrosion inhibitors, this explanation has been confirmed by the open circuit potential and potentiodynamic scan methods and enhanced with (EIS) measurements. The data demonstration the "charge transfer resistance" and the "electrical double layer capacitance" have minimum values due to the adsorption of the aminobenzylpenicillin and cefixima molecules on the carbon steel electrode.

3. The results of the "Langmuir adsorption isotherm" and (SEM) images suggest that the corrosion inhibition mechanism occurs chiefly by adsorption then forms a protective layer on the electrode surface. Thermodynamic and activation energy parameters were appreciated and elucidate the strong adsorption of aminobenzylpenicillin and cefixima inhibitors.
4. Theoretical calculations were performed on the drug inhibitors to determine some of electronic properties such as E_{HOMO}, E_{LUMO}, distribution atomic charge, molecular surface area, and binding energy were shown to be in good agreement with experimental evidences to support the suggestion that both drug inhibitors could also be used as corrosion inhibitors.

دراسة تثبيط تآكل حديد الصلب الكربوني في الوسط ألحامضي باستخدام مركبات صديقة للبيئة

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الخلاصة

أن الدراسة الحالية تضمنت دراسة التأثير التثبيطي للمركبات الدوائية للسفكيزيم والامينو بنزيل بنسلين في وسط حامضي من حامض الكبريتيك الخالٍ من الأوكسجين لأنموذج من حديد الصلب الكربوني باستخدام التقنيات الكهروكيميائية مُعززة بحسابات ميكانيك الكم وصور المجهر ألللالكتروني الماسح لدراسة مورفولوجية سطح القطب العامل. بينتْ النتائج التجريبية بأن المركبات الدوائية قيد الدراسة تسلك كمثبطات جيدة لعملية التآكل وكبح التفاعلات الانودية – الكاثودية (مزدوجة التثبيط). أن النسبة المئوية لكفاية حماية التآكل تزاد مع زيادة تركيز المثبطات للسفكيزيم والامينو بنزيل بنسلين. خُضعتْ حركيات تفاعلات التآكل لمعادلة آرينوس وحُسبتْ قيم طاقة التنشيط بغياب ووجود مثبطات للسفكيزيم والامينو بنزيل بنسلين، بينتْ النتائج أن كفاية تثبيط التآكل بوجود المثبطات تقل مع زيادة درجة الحرارة. قُدرتْ المتغيرات الثرموديناميكية لعملية تثبيط التآكل لأنموذج من حديد الصلب الكربوني وأطاعتْ عملية أمتزاز مثبطات السفكيزيم والامينو بنزيل بنسلين معادلة لنكماير على سطح القطب من خلال تكوين طبقة حماية لوُحظتْ من خلال دراسة مورفولوجية سطح القطب باستخدام المجهر الالكتروني الماسح. حُسبت أهم الخصائص الالكترونية من خلال حسابات ميكانيك الكم للتراكيب الكيميائية للمثبطات المستخدمة ونوقشتْ نتائجها وبينت مدى ترابطها مع النتائج التجريبية.

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