Inhibition Potentials and Adsorption Performance of Two Sulfonylurea Antibiotic Expired Drugs on the Corrosion of Mild Steel in 0.5 M H$_2$SO$_4$

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The inhibition potentials of expired glibenclamide (Glib) and glimepiride (Glim) as two significant sulfonylurea antibiotic drugs on the corrosion behavior of mild steel in 0.5 M sulfuric acid solution were explored using different chemical and electrochemical ways. As the concentration of the expired drugs increases, the weight loss, corrosion current density and the capacity of double layer decrease while the values of charge transfer resistance, surface coverage and the percentage inhibition efficiency augment, indicating that the inhibitory impact of both expired Glib and Glim. The percentage inhibition efficiency increases with decrease in temperature. The inhibition was interpreted by the spontaneous adsorption of the two expired drugs on the mild steel surface by increasing the number of adsorbed particles that cover the largest area of the metal by constructing a barrier layer between the steel surface and the corrosive acid solution. The adsorption process is subject to Langmuir isotherm. Potentiodynamic polarization data demonstrate that both expired drugs act as mixed inhibitors. The activation and adsorption thermodynamic parameters were evaluated and suggest the physical adsorption of the examined drugs

1. INTRODUCTION

Mild steel is one of the supreme important metals that have multiple applications in the industry. Sulfuric acid is usually used to clean mild steel by removing deposits formed throughout pickling and chemical cleaning, and acidification of an acid oil well [1-3]. Unfortunately, acidic solutions cause corrosion to steel and thus cause great material losses affecting the national economy of any country. Therefore, scientists in this field have turned to solve these national problems and found that one of the

most important and most effective of these solutions and economically profitable is the use of corrosion inhibitors.

In previous studies, scientists used organic compounds that contain some atoms, such as oxygen, nitrogen, or sulfur, through which they form chemical bonds that facilitate the process of forming an adsorbed layer on the steel surface that separates the metal from the corrosive solution, thereby reducing the rate of corrosion and increasing the life span of the metal, and thus solving the problem of corrosion [4-15]. Most of the organic compounds used as corrosion inhibitors give high inhibition efficiency, but unfortunately, most of these compounds are toxic and harmful to the environment in addition to the high price, which is not economically beneficial.

In recent years scientists have used pharmaceutical drugs, especially expired ones, to inhibit the corrosion of most metals and alloys [16-25]. They gave a high inhibitory efficiency, environmentally friendly, nontoxic, relatively cheap and economical was very beneficial because it was used instead of culling it.

This study aims to solve the problem of corrosion of MS in 0.5 M H_2SO_4 solution by expired glibenclamide (Glib) and glimepiride (Glim) drugs using weight loss (WL), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) measurements. Also, study the effect of rising the temperature and determine the thermodynamics of the activation and adsorption process was explained.

2. EXPERIMENTAL METHODS

2.1. Chemical Composition of Mild Steel (MS)

The chemical composition of the inspected MS alloy in percentage weight is: 0.07C, 0.27Mn, 0.012S, 0.021P, 0.07Si and the rest is Fe.
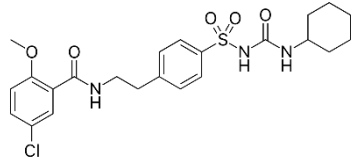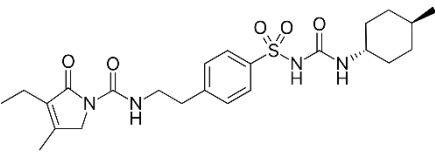
2.2. Inhibitors and Solutions

The utilized expired sulfonylurea antidiabetic drugs, glibenclamide (Glib) and glimepiride (Glim), as inhibitors of the corrosion of MS in 0.5 M H_2SO_4 solutions were purchased from Pfizer pharmaceutical company. The trade names, chemical structures, molecular formulas and molecular weights of such drugs are listed in Table 1. Solutions of expired drugs were freshly prepared by dissolving weighed amount of their samples in bidistilled water. H_2SO_4 corrosive solution were prepared by dilution of 99% H_2SO_4 (Merck) utilizing bidistilled water.

2.3. Methods

The inhibition efficiencies of the examined expired drugs were studied utilizing weight loss (WL) measurements as a chemical technique and potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) methods as electrochemical ones. All measurements were conveyed out

in a temperature-controlled system. MS samples utilized for WL measurements were cylindrical rods of areas of about 14 cm^2 which were prepared for such measurements as reported earlier [5,10]. Both PP and EIS were carried out using PGSTAT30 potentiostat/galvanostat in a three-electrode cell. The working electrode (WE) had a rod from the investigated MS sample which was inserted into a Teflon holder and the exposed electrode area to the corrosive solution was 0.5 cm^2. Before each experiment the WE was prepared as in WL measurements, then it was put into the glass cell. PP curves were acquired by automatically altering the electrode potential at a scan rate of 2.0 mV/s and repeated 3 times to check the reproducibility of the results. EIS measurements conveyed out in a frequency range of 100 kHz to 0.1 Hz with an amplitude of 4.0 mV peak-to-peak using AC signals at OCP.

Table 1. Trade names, chemical structures, molecular formulas and molecular weights of glibenclamide and glimepiride drugs.

Drug name	Glibenclamide	Glimepiride
Trade name	Diabeta	Amaryl
Abbreviation	(Glib)	(Glim)
Chemical structure		
Chemical formula	C$_{23}$H$_{28}$ClN$_3$O$_5$S	C$_{24}$H$_{34}$N$_4$O$_5$S
Mol. weight, g. mol^{-1}	494.04	490.62

3. RESULTS AND DISCUSSION

3.1. Weight-Loss Measurements and the Effect of Temperature

Figure 1 represents the WL - inundation time curves for MS rods in blank 0.5 M H$_2$SO$_4$ solution and includes various concentration expired antibiotics drugs namely, Glib and Glim. Obviously from this Fig., the WL of mild steel reduced with rising the concentration of the two expired dugs. This demonstrates that these two investigated expired drugs inhibit the corrosion of mild steel in 0.5 M H$_2$SO$_4$ solution. The above relationship donates a linear change indicating the absence of an insoluble membrane during the dissolution of the steel. In the absence of any superficial membranes, the drug is first adsorbed on the surface of the steel and imeding the dissolution process, either by blocking the reaction sites or by altering the mechanism of the partial anodic and cathodic processes.

The corrosion parameters derived from the WL measurements such as, the corrosion rate (CR.), the inhibition efficiency (%IE) and the surface coverage (θ) was computed by applying the next equations

$$CR = \Delta W/At \qquad\qquad\qquad (1)$$

$$\% \ IE = \theta \ x \ 100 = \left[1 - \frac{CR_{inh}}{CR} \right] x \ 100 \qquad (2)$$

where, (ΔW) is the change in the WL of mild steel rod before and after immersing in the tested inhibitory solution,(t) is the time in hours and (A) is the surface area of mild steel rod in cm^2. CR and CR$_{inh}$ are corrosion rates of free acid solution and contains the two expired drugs (Glib & Glim), respectively.

The corrosion parameters such as CR, % IE and θ acquired from the WL measurements were registered in Table 1. Clearly this table, as the concentration of the two expired drugs increases, the values of CR reduced and the values of % IE increase, suggesting the inhibitory impact of the tested the two expired drugs and the order of %IE decreases in the following order: Glim > Glib . This order will be discussed later.
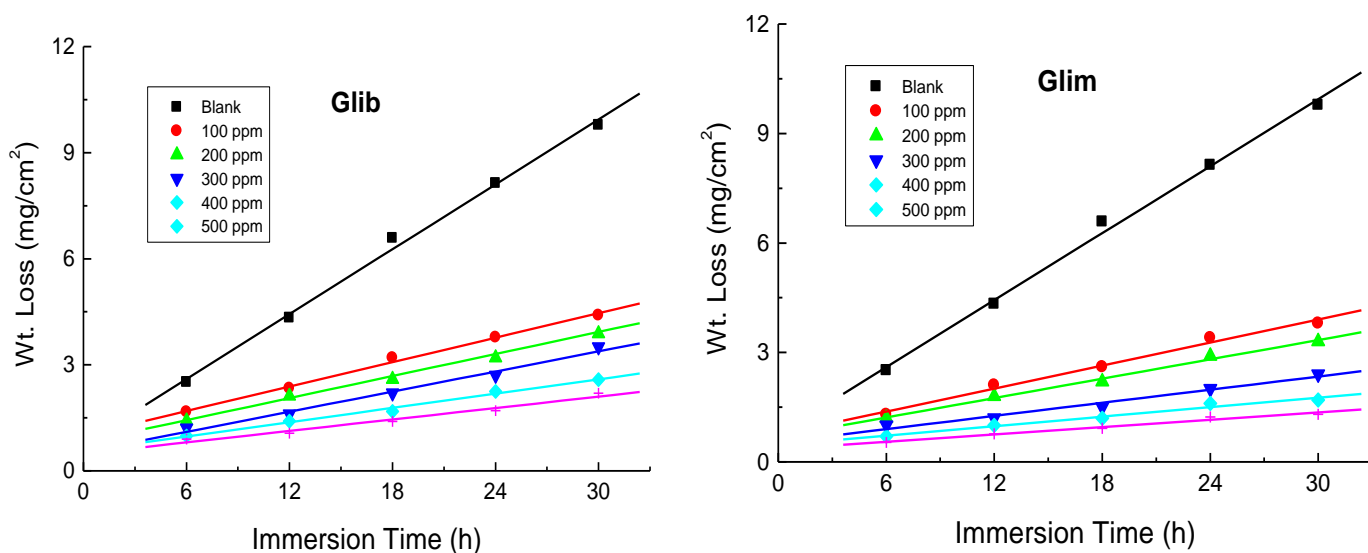

Figure 1. Weight-loss versus inundation time for MS in 0.5 M H$_2$SO$_4$ solution in the absence and presence of different concentrations of glibenclamide (Glib) and glimepiride (Glim) at 298 K.

Table 1. Values of CR of MS, % IE and θ of several concentrations of glibenclamide (Glib) and glimepiride (Glim) in 0.5 M H$_2$SO$_4$ solution at various temperatures.

Inhibitor	Inhibitor Concn. (ppm)	Temperature (K)											
		288			**298**			**308**			**318**		
		CR	% IE	θ	CR	% IE	θ	CR	% IE	θ	CR	% IE	θ
Blank	**0**	103	--	--	124	--	--	139	--	--	157	--	--
Glib	**100**	42	59.2	0.59	57	54.0	0.54	68	51.1	0.51	82	48.6	0.48
	200	30	70.9	0.71	40	67.7	0.68	51	63.4	0.63	64	59.4	0.59
	300	19	81.5	0.82	27	78.3	0.78	35	74.8	0.75	46	70.5	0.71
	400	14	86.4	0.86	21	83.1	0.83	29	79.2	0.79	39	75.3	0.75
	500	11	89.3	0.89	17	86.3	0.86	25	82.0	0.82	35	77.5	0.78
Glim	**100**	36	65.0	0.65	50	59.6	0.60	64	54.1	0.54	77	50.9	0.51
	200	25	76.1	0.76	35	71.7	0.72	46	67.2	0.67	58	63.1	0.63
	300	18	83.3	0.83	25	80.1	0.80	35	74.7	0.75	44	72.0	0.72
	400	12	87.8	0.88	20	83.8	0.84	28	79.8	0.80	36	77.1	0.77
	500	9	91.2	0.91	17	86.3	0.86	24	82.6	0.83	31	80.4	0.80

The effect of rising temperature from 288 K to 318 K on the corrosion parameters of mild steel in blank 0.5 M H_2SO_4 solution and the presence of various concentrations of Glib and Glim was studied and registered in Table 1. It is clear that as the temperature rises the CR increases while the values of %IE and θ are lowered suggested the adsorption of expired drugs Glib and Glim on the mild steel surface is physical [26,27].

3.1.2. Adsorption Isotherm

The tested expired drugs inhibit the corrosion of mild steel in 0.5 M H_2SO_4 solution by its adsorption. The adsorption was accompanied by desorption of water molecules from the surface. The adsorption process can be considered as replacement operation in which the expired drug molecule (Ex-D) in the aqueous phase substitutes an "y" adsorbed on the steel surface according to the following equation:

$$Ex\text{-}D_{(aq)} + yH_2O_{(sur)} \longrightarrow Ex\text{-}D_{(sur)} + nH_2O_{(aq)} \qquad (3)$$
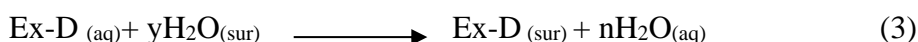
where, y the number of water molecules replaced by one expired drug.

To find the appropriate adsorption isotherm, the surface coverage values (θ) for various concentrations of expired drugs (Glib and Glim) are entered into various adsorption isotherms. Langmuir isotherm was found to be the best description of adsorption behavior of the tested expired drugs on mild steel surface by applying the following equation [28]:

$$C_{inh} / \theta = 1 / K_{ads} + C_{inh} \qquad (4)$$

where, C_{inh} is the concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process and (θ) is the fraction of surface coverage.

Figure 2 displays the relationship between C_{inh} / θ versus C_{inh} for the adsorption of expired Glib and Glim drugs on the mild steel surface in 0.5 M H_2SO_4 solution at different temperatures. Straight lines were obtained with intercept equal to $1/K_{ads}$. and slope approximately equal to the unit indicating that the adsorption of the expired Glib and Glim drugs on the mild steel surface follows the Langmuir isotherm. This isotherm postulates that there is the absence of the interaction between adsorbed molecules [29].

The free energy of adsorption (ΔG^o_{ads}) was computed from the next equation [30,31]:

$$\exp(-\Delta G^{\circ}_{ads}/RT) = 55.5K_{ads}. \qquad (5)$$

where, the value (55.5) is the molar concentration of water in solution in molarity (mol L^{-1}). The computed values of K_{ads} and ΔG^o_{ads} at different temperature were registered Table 2. From the values of K_{ads} and the negative values of ΔG^o_{ads} denoting the strong spontaneous and a highly efficient adsorption of expired Glib and Glim drugs on the MS surface in 0.5 M H_2SO_4 solution at different temperatures. It was reported that [32] The Values of ΔG^o_{ads} up to -20 kJ mol^{-1} or numerically lower were consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physical adsorption); Whereas those equal -40 kJ mol^{-1} or numerically higher are involved sharing or transporting a lone pair of electrons from the organic molecules to the metal surface to form a coordinate type of bond (chemical absorption). The values of ΔG^o_{ads} in Table 2 ranged from -30.75 to -32.46 kJ mol^{-1} indicating that the adsorption expired Glib and Glim drugs on the MS surface in 0.5 M H_2SO_4 at different temperature is physical adsorption.
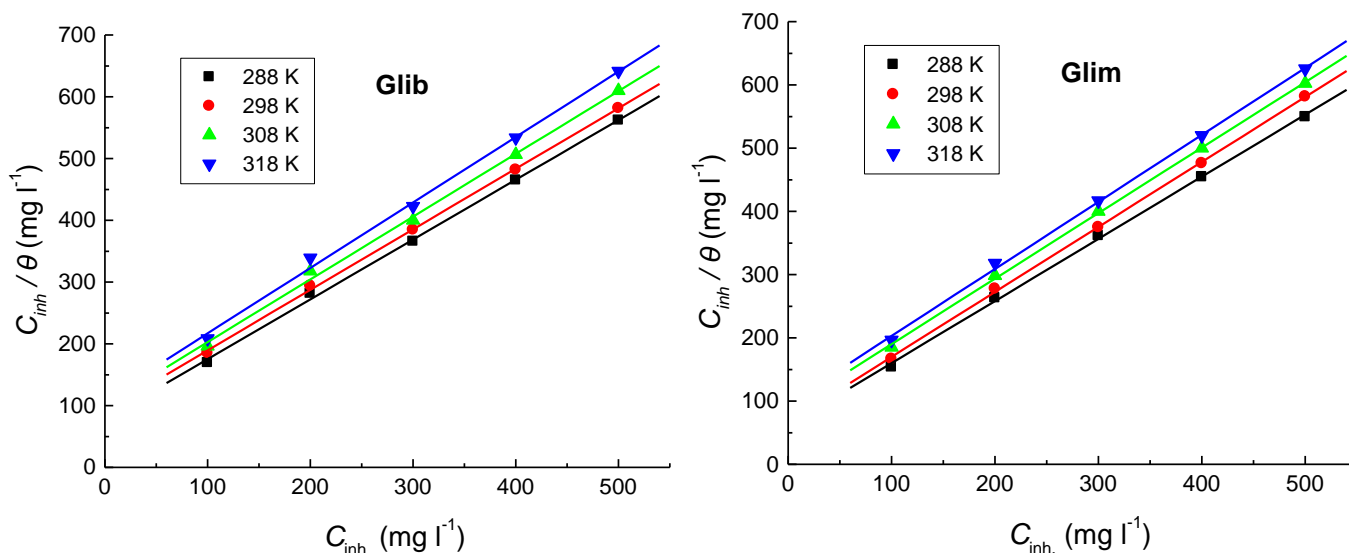
Figure 2. Langmuir adsorption isotherms for glibenclamide (Glib) and glimepiride (Glim) adsorbed on MS surface in 0.5 M H_2SO_4 solution at different temperatures.

The enthalpy of adsorption (ΔH^o_{ads}) can be computed from the Van't Hoff equation [33]:

$$\ln K_{ads} = \frac{-\Delta H^o_{ads}}{RT} + C \qquad (6)$$

where, C is constant, Fig.3 represents the relation between ln K_{ads} against 1/T for the adsorption of expired Glib and Glim drugs on the MS surface in 0.5 M H_2SO_4 solution. Straight lines were obtained. The ΔH^o_{ads} values were evaluated from the slopes and recorded in Table 4. It was observed that the values of ΔH^o_{ads} are negative reveal that the adsorption expired Glib and Glim drugs on the mild steel surface are exothermic process with physisorption [34].
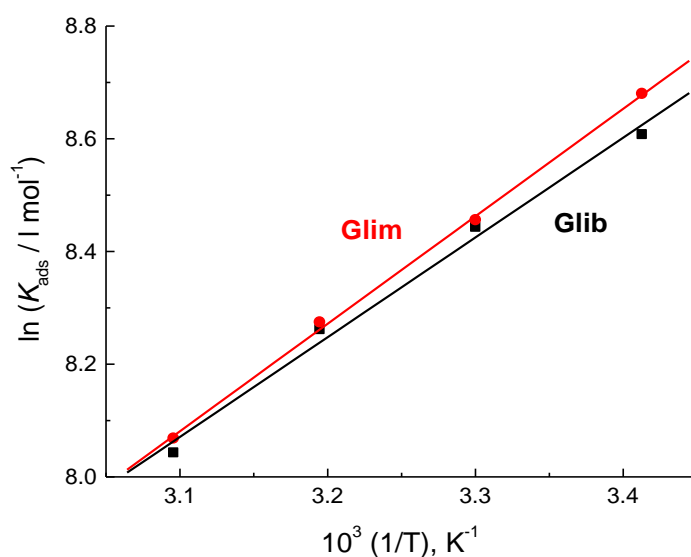

Figure 3. Van't Hoff plots for glibenclamide (Glib) and glimepiride (Glim) adsorbed on MS surface in 0.5 M H_2SO_4.

Table 2. Values of thermodynamic parameters and adsorptive equilibrium constant (K_{ads}) for the corrosion of MS in 0.5 M H_2SO_4 solution in the presence of glibenclamide (Glib) and glimepiride (Glim) at different temperatures.

Blank +	Temp. (K)	$10^{-3} K_{ads}$ l mol^{-1}	ΔG^o_{ads} kJ mol^{-1}	ΔH^o_{ads} kJ mol^{-1}	ΔS^o_{ads} J mol^{-1} K^{-1}
Glib	**288**	5.47	-30.75	-14.71	55.69
	298	4.64	-31.39		55.97
	308	3.87	-31.95		55.98
	318	3.11	-32.38		55.57
Glim	**288**	5.88	-30.93	-15.88	52.26
	298	4.70	-31.42		52.15
	308	3.92	-31.99		52.31
	318	3.19	-32.46		52.14

The adsorption entropy (ΔS^o_{ads}) can be determined from Gibbs–Helmholtz equation:

$$\Delta S^o_{ads} = (\Delta H^o_{ads} - \Delta G^o_{ads}) / T \qquad (7)$$

The computed values of ΔS^o_{ads} are registered in Table 4. It is found that, the values of ΔS^o_{ads} are positive donating an increase in disturbance during the adsorption of expired Glib and Glim drugs on the mild steel surface [35].

3.1.4. Thermodynamic Activation Parameters

The activation energy (E_a) values of mild steel corrosion in bank 0.5 M H_2SO_4 solution and contains various concentrations of expired Glib and Glim drugs were determined from Arrhenius equation [36,37].

$$\ln CR = \ln A - (E_a / RT) \qquad (8)$$

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

Figure 4 represents the Arrhenius plots (ln CR versus 1/T) for mild steel corrosion in blank 0.5 M H_2SO_4 solution and contains various concentrations of expired Glib and Glim drugs. Straight lines were obtained with slope equal to (-E_a/R). The Ea values were computed and inserted in Table 3 The data show that the E_a values in the presence of various concentrations of expired Glib and Glim drugs are greater than that of the blank acid solutions, indicating that the adsorption of these inhibitors molecules on the metal surface is considered to be physical adsorption [35]. The presence of expired drugs encourages an energy barrier for the dissolution reaction and this barrier increases with rising the concentration of these drugs.
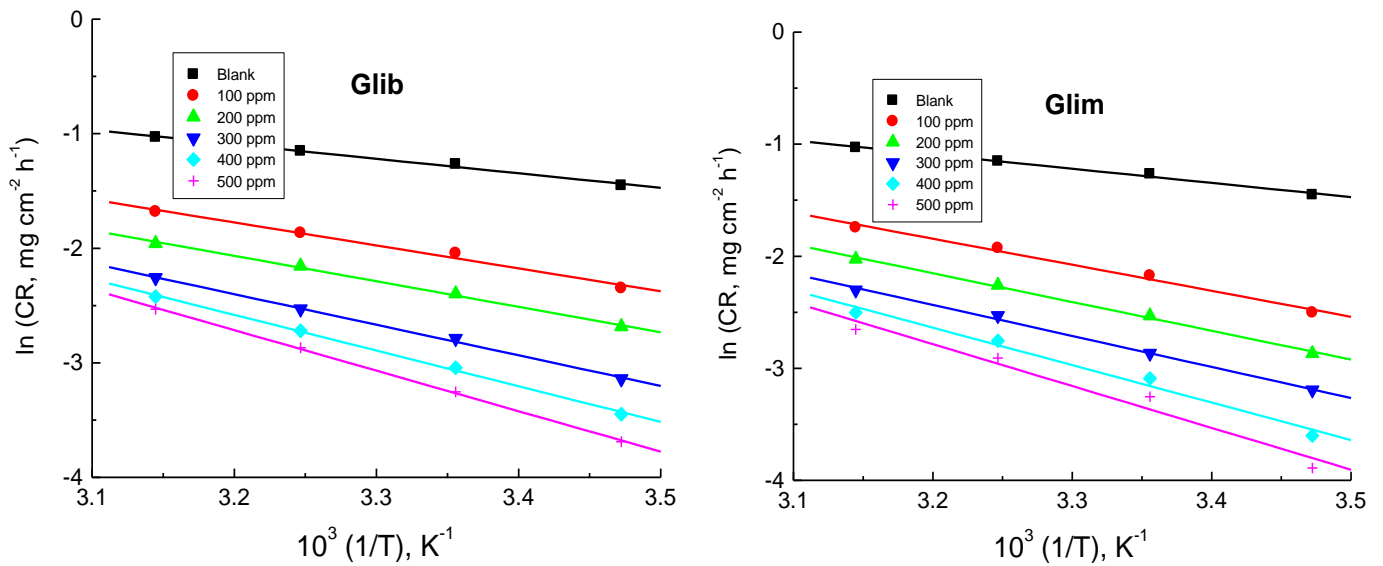
Figure 4. Arrhenius plots for the corrosion of MS in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of glibenclamide (Glib) and glimepiride (Glim).

The thermodynamic activation energy of enthalpy (ΔH^*) and entropy (ΔS^*) were calculated determined from the transition state theory.[36,37]

$$\ln (CR/T) = [\ln (R / N_A h) + (\Delta S^*/ R)] - (\Delta H^* / RT) \qquad (9)$$

where, h is the Plank constant, N_A is the Avogadro's number.

Table 3. Activation parameters for mild steel corrosion in 0.5 M H₂SO₄ solution in the absence and presence of several concentrations of glibenclamide (Glib) and glimepiride (Glim).

Inhibitor	Inhibitors Concn. (mg l⁻¹)	E_a^* kJ mol⁻¹	ΔH^* kJ mol⁻¹	ΔS^* J mol⁻¹ K⁻¹
Blank	**0**	**10.81**	**7.98**	**-184.98**
Glib	**100**	17.21	14.13	-195.37
	200	19.12	15.96	-192.88
	300	22.86	19.70	-183.74
	400	26.69	23.45	-172.93
	500	30.35	26.85	-162.95
Glim	**100**	19.95	16.63	-187.89
	200	22.03	18.79	-184.15
	300	23.78	20.45	-181.24
	400	28.68	24.94	-167.61
	500	32.09	28.52	-158.38

Figure 5 represent the transition state plots for the corrosion of MS in free 0.5 M H$_2$SO$_4$ solution and in the presence of expired Glib and Glim drugs. A straight lines were obtained with slope equal to (-ΔH*/R) and intercept of ln (R / N$_A$h) + (ΔS*/ R). Values of ΔH* and ΔS* were calculated and listed in Table 3.

The positive sign of the enthalpy of activation (ΔH*), means the endothermic nature of the corrosion process. This indicates that the corrosion of mild steel is difficult in the presence of the tested expired drugs. The negative sign of entropy of activation (ΔS*), indicates that the activated complex in the rate determining step represents an association rather than dismantling, reflecting that an increase in order occurs, moving from reactant to activate complex [38,39].
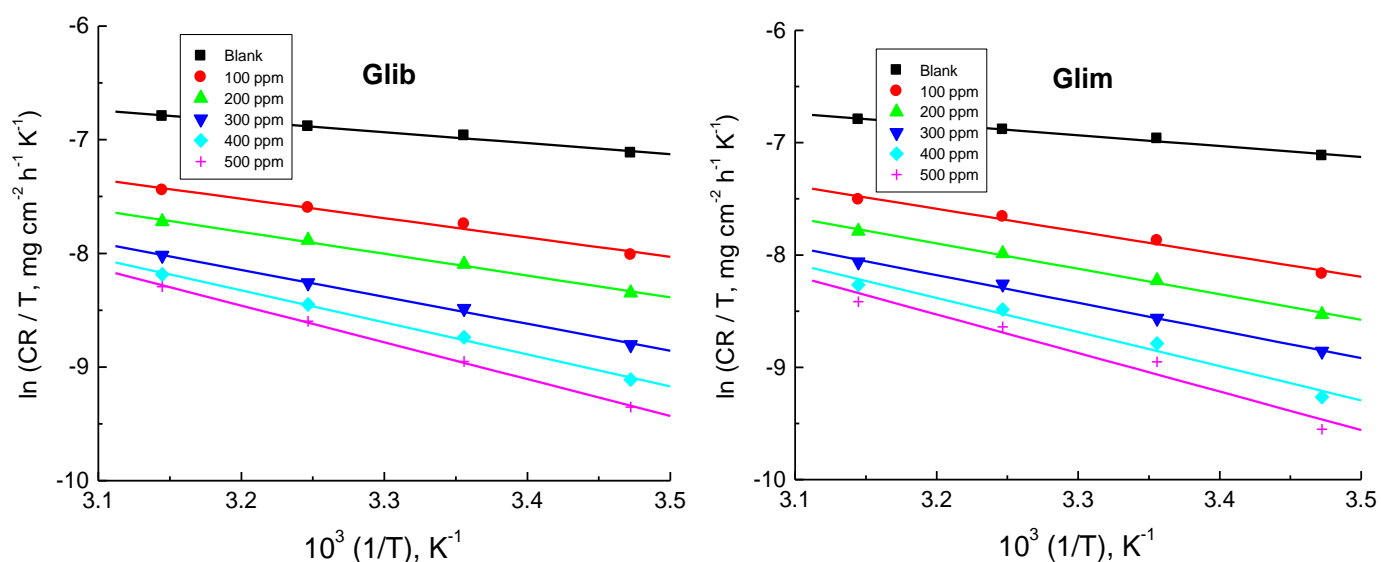

Figure 5. Transition state plots for the corrosion of MS in 0.5 M H$_2$SO$_4$ solution in the absence and presence of glibenclamide (Glib) and glimepiride (Glim).

3.2. Potentiodynamic Polarization (PP) Measurements

PP curves of the MS in a free 0.5 M H$_2$SO$_4$ solution and includes various concentration expired drugs namely Glib and Glim at a scan rate 2 mVsec^{-1} are shown in Fig.6. From this figure it is evident that the anode and cathode polarization curves shift towards the low current density values when adding the expired tested drugs. This outcome indicates the inhibitory effect of the tested drugs on the corrosion of MS in a 0.5 M H$_2$SO$_4$. Some corrosion kinetic parameters such as anodic (β_a) and cathodic (β_c) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (I_{corr}) and inhibition efficiency (%IE) were derived from the curves and inserted in Table 4. Inspection of Table 4, upon the addition of increasing concentrations of the expired Glib and Glim, it is clear that:

1. Both β_a and β_c Tafel constants are approximately constant, which means that the expired drugs are classified as a mixed type inhibitor by adsorption at both anodic and cathodic sites on the steel surface and thus delay both the anodic dissolution of the steel and cathodic hydrogen evolution reactions.

2. E_{corr} values are almost constant and are not affected by the addition of the examined expired drugs.

3. I_{corr} decreases, and the %IE increases, indicating the inhibitory action of the examined two expired drugs due to the formation of insoluble layer resulting from the adsorption of drug molecules on the surface of mild steel.

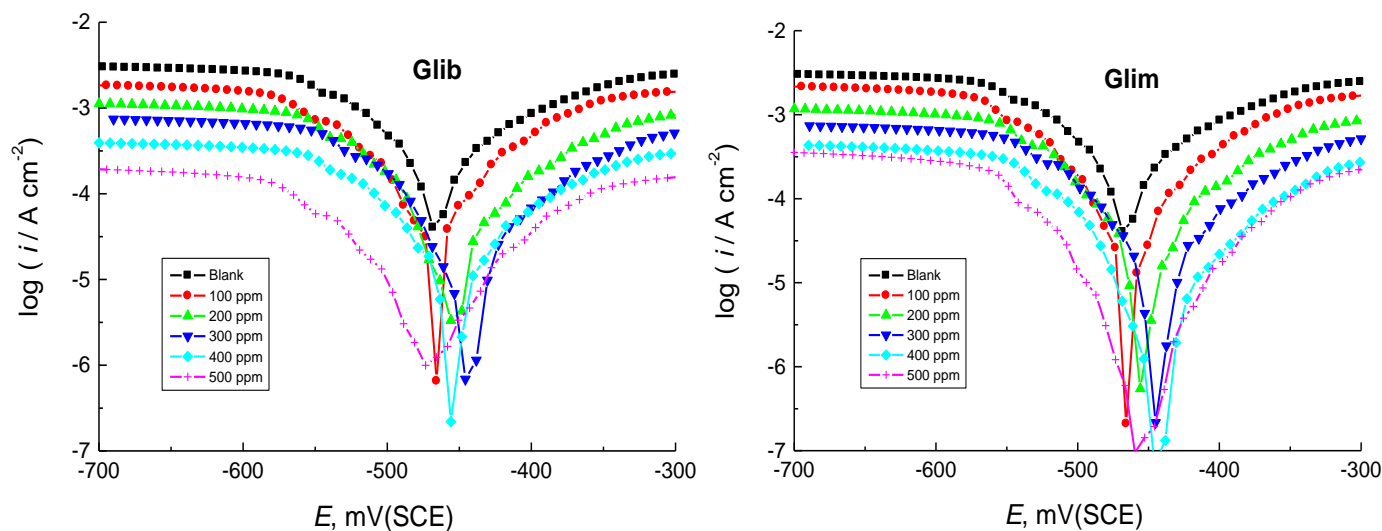4.   The sequence of %IE decreases in the following order: Glim > Glib.

Figure 6. PP curves for MS corrosion in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of glibenclamide (Glib) and glimepiride (Glim) at 298 K.

Table 4. PP data for the corrosion of MS in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of glibenclamide (Glib) and glimepiride (Glim) at 298 K.

Inhibitor	Inhibitor Conc. (ppm)	$-E_{corr}$ (mV(SCE))	β_a (mV/decade)	$-\beta_c$ (mV/decade)	i_{corr} ($\mu A/cm^2$)	% IE
Blank	**0**	**468**	**86**	**91**	**208**	**--**
Glib	100	466	81	86	98	52.9
	200	460	80	90	64	69.2
	300	457	77	92	48	76.9
	400	448	82	93	37	82.2
	500	469	80	89	31	85.1
Glim	100	469	78	84	81	61.1
	200	458	82	91	56	73.1
	300	447	80	93	37	82.2
	400	445	76	91	29	86.1
	500	459	71	84	25	88.0

3.3. EIS Measurement

The Nyquist diagrams of the mild steel in a free 0.5 M H_2SO_4 solution and includes some concentration ranged from (100-500 ppm)of the expired drugs namely, Glib and Glim at 298° K are shown in Fig.7. From this figure it is evident that the Nyquist plots are not an ideal semicircle as expected from the theory of EIS.
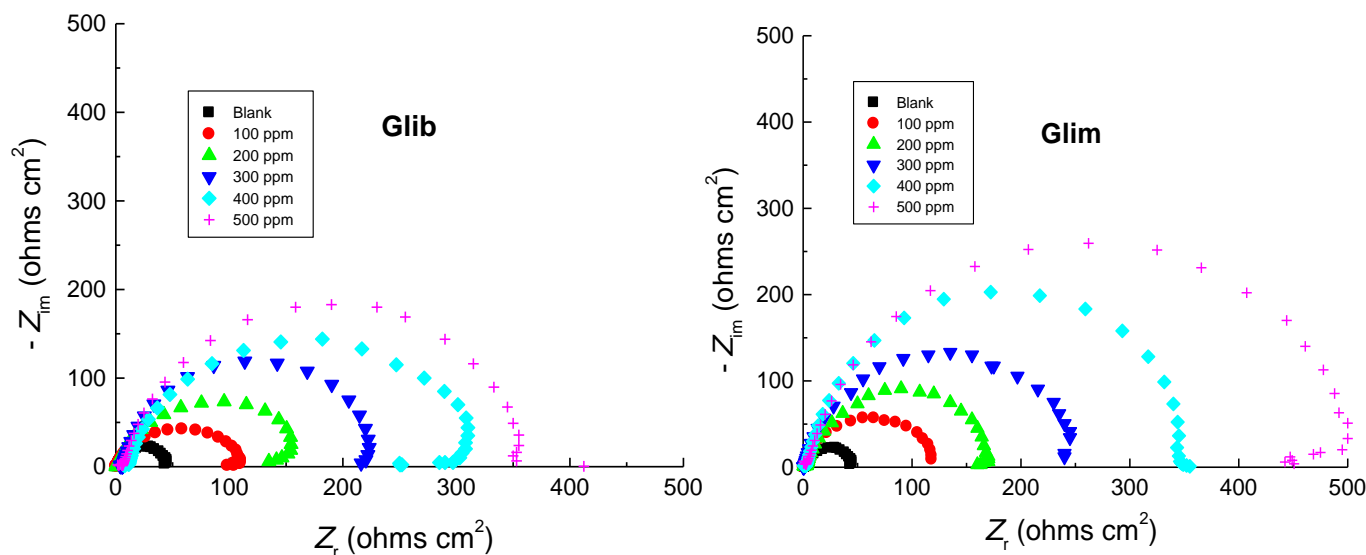
Figure 7. Nyquist plots for the corrosion of mild steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of glibenclamide (Glib) and glimepiride (Glim) at 298 K.

This is due to the frequency dispersion as a result of roughness and in homogeneity of the steel surface [40-42]. As the concentration of expired drugs increases, the diameters of the semicircles increase, which proves the increase in the protective properties of the surface of the mild steel. Thus, the capacitive semicircle is associated with the dielectric properties and the thickness of adsorbent membrane. Nyquist plots were analyzed by installing the acquired data to a parabolic circuit model illustrated in Fig. 8 [42].
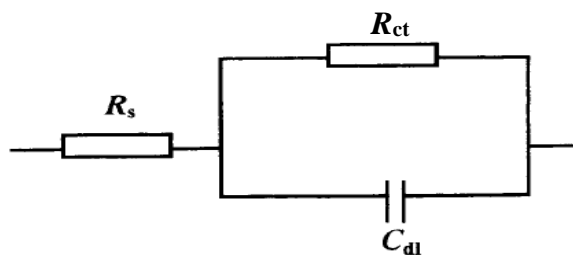
Figure 8. The equivalent circuit model used to fit the experimental results.

The main parameters extracted from the Nyquist diagram analysis are the charge transfer resistance R_{ct} (high frequency loop diameter) and the capacity of the double layer C_{dl} which is defined as follows:

$$C_{dl} = \frac{1}{2\pi\, f_{max}\, R_{ct}}$$ (10)

The % IE deduced from the EIS measurements are computed from the following relation:

% IE = (1- $R_{ct\text{-}un}$ / $R_{ct\text{-}in}$) 100   (11)

where, $R_{ct\text{-}un}$ and $R_{ct\text{-}in}$ are the charge transfer resistance in the uninhibited and inhibited solution respectively. The electrochemical parameters extracted from EIS measurements such as C_{dl}, R_{ct} and %IE are included in Table 5. Examination of the parameters obtained in Table 2. It evident that, with increasing concentration of expired Glib and Glim, R_{ct} values have increased due to the formation of a protective layer arises from the adsorption of the drugs on the surface of mild steel [43.44]. C_{dl} values are decreased due to the substitution of the water molecule by adsorbing of the expired drug on the steel surface. This reduced the local dielectric constant of the metal solution/interface [45].The order of %IE decreases in the following order: Glim > Glib.

It is important to mention here that this sequence is the same as that obtained from the results of WL and PP measurements. This finding reflects the resulting harmony between the three techniques used to calculate the efficacy of inhibition, thus demonstrating the validity and accuracy of the results obtained.

Table 5. Values of C_{dl}, R_{ct}, %IE and θ of several concentrations of glibenclamide (Glib) and glimepiride (Glim) for MS corrosion in 0.5 M H_2SO_4 solution at 298 K.

Inhibitor	Inhibitor Concn. (ppm)	C_{dl} ($\mu F\ cm^{-2}$)	R_{ct} ($\Omega\ cm^2$)	% IE
Blank	0	65	48	--
Glib	100	56	107	55.1
	200	48	157	69.4
	300	42	225	78.7
	400	37	308	84.4
	500	30	355	86.5
Glim	100	52	121	60.3
	200	45	170	71.8
	300	40	241	80.1
	400	33	349	86.2
	500	26	498	90.4

3.5. Mechanism of Corrosion Inhibition

The inhibition power of expired drugs namely, Glib and Glim for the corrosion of mild steel in 0.5 M H_2SO_4 solution using WL, PP and EIS ways are mainly due to their adsorption. The adsorption process depended on several factors as nature of the metal, the kind of the aggressive acidic solutions, the temperature, the chemical composition of the additive, the presence of some heteroatom, the occurrence of electro donating or repelling groups in the chemical structure and other several factors. In

light of the chemical structure of the expired drugs that have been examined, we find that they have many advantages and factors that facilitate the adsorption process, resulting in a high value of the inhibition efficiency. The presence of these drugs led to WL, I_{corr} and C_{dl} resulted in a decrease while R_{ct}, θ and %IE increased, indicating that the inhibitory impact of the two tested drugs. %IE increases with increased concentration of expired drugs. These results can be attributed to the fact that, as the concentration of the drug augments, the number of adsorbed particles increases which leads to covering a greater area of the metal by forming a barrier layer between the surface of the steel and the acidic corrosive solution. This formed layer prevents the mass and charge transformation between the steel and its. Therefore, the inhibition efficiency depends on the fraction of the metal surface covered by the adsorbed layer as well as its stability. This is due to an increase of molecular weight of the Glib and Glim are equal 494.04 and 490.62 g. mol^{-1}, respectively. Thus, the CR decreases, and the %IE increases. The N and O atoms occurred in the chemical structure of the drugs act as the active center to facilitate the adsorption process. It is clear from the results obtained that the %IE is fairly close to the two expired drugs used, due to the approximate molecular weight of each and the presence of the same effective groups.

4. CONCLUSIONS

1. Expired Glib and Glim drugs worked as an efficacious inhibitors for the corrosion of MS in 0.5 M H_2SO_4, solution.

2. The inhibition efficiency augments with increased the examined Glib and Glim drug concentrations and with lowering temperature.

3. The inhibition impact of Glib and Glim due to their spontaneous adsorption on the surface of mild steel.

4. Adsorption of Glib and Glim drugs onto the surface of MS obeys Langmuir isotherm

5. PP parameters demonstrate that both expired Glib and Glim drugs act as mixed inhibitors

6. The thermodynamic parameters indicate prove that the adsorption is physical and endothermic nature

7. The %IE obtained from the three techniques employed is approximately consistent with each other.

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