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Streptoquin and Septazole: Antibiotic Drugs as Corrosion Inhibitors for Copper in Aqueous Solutions

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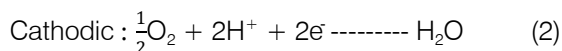
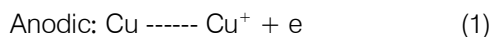
A. S. Fouda ^α & H. E. Gadow ^σ

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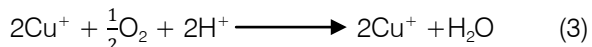
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I. INTRODUCTION

Acid solutions are widely used in different industries. The most important fields of application are acid pickling, industrial acid cleaning, acid descaling [1]. copper is a metal that has been widely used in different types of industries, including electronics due to its relatively high corrosion resistance. Its protection against corrosion saves large costs on repairs and equipment replacements. In spite of copper being a relatively noble metal, it reacts easily in a medium containing oxygen. It has long been known that when copper corrodes in aerated, chloride containing solutions, a layer of Cu_2O is formed on the surface of the metal. In addition, copper is dissolved by reactions which can be summarized as follows [2] :



Then in solution:



At chloride concentrations lower than 1 M, the copper dissolution occurs through the formation of CuCl , which is not protective enough and is converted to soluble CuCl_2 by reacting with excess chloride [3]. According to Bacarella and Griess [4], the anodic dissolution of copper is under mixed control by the

electrodissolution of copper and the diffusion of soluble CuCl_2 from the Helmholtz plane into the bulk solution. On the other hand-higher chloride complexes such as CuCl_3^{2-} and CuCl_4^{3-} are formed in addition to CuCl and CuCl_2 at chloride concentrations higher than 1M [5]. One of the most important methods in the protection of copper against corrosion is the use of organic inhibitors. Organic compound containing polar groups including nitrogen, sulfur and oxygen[6-18] have been reported to inhibit copper corrosion. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functions groups are regarded as the reaction center that stabilizes the adsorption process[19]. In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of the electrolyte solution[20]. Also, heterocyclic compounds containing nitrogen are known to be good inhibitors of copper and alloys [21]. As the awareness of environment protection, the research is oriented to the development of environmental-friendly corrosion inhibitors[22-25]. Seeking for alternatives of toxic inhibitors is under consideration. Some studies used drugs as green corrosion inhibitors for various metals and alloys[26-30].The use of environmental friendly pharmaceutical compounds (streptoquin and septazole) as corrosion inhibitors for copper has not been reported before. So, our aim is to study the inhibiting effect of these drugs on copper corrosion in HCl solution using various electrochemical techniques.

II. EXPERIMENTAL

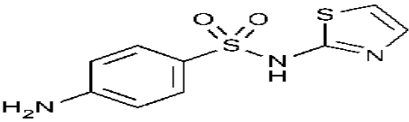
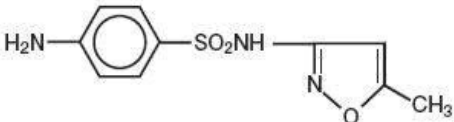
a) Materials and Solutions

Copper was used as the metal electrode for corrosion studies and its chemical composition As follows (weight %): Ni 0.54, Fe 0.066 other impurities 0.76% and Cu 98.04 %. The investigated compounds are belonged to the sulfa group (streptoquin & septazole). As shown in Table 1. These drugs were obtained from Glaxo SmithKline, Medical Union Pharmaceuticals, Alexandria Co. for Pharmaceuticals, Egypt. Analytical grade HCl (37 %) was used as corrosive solution. Double distilled water was used throughout experiments for the preparation of solutions.

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Table 1: Names, structural and molecular formulas and molecular weights for of the investigated drugs

Names	Structures,	Mol.formulas & Mol. Wt.
Streptoquin Benzenesulfonamide, 4-amino-N-2-thiazolyl- N1-2-Thiazolylsulfanilamide		C ₉ H ₉ N ₃ O ₂ S ₂ 255.32
Septazole M1-(5-methyl-3-isoxazolyl) sulfanilamide		C ₁₀ H ₁₁ N ₃ O ₃ S 268.28

b) Methods and Techniques

Polarization experiments were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form of disc cut from copper with dimension 1x1 cm which embedded in epoxy with resin of polytetrafluoroethylene. Before measurement, the exposed surface was wet-polished with silicon carbide abrasive paper (800, 1000, 1200 grit), then the electrode was immersed in solution at natural potential until a steady state was reached. All experiments were carried out in freshly prepared solutions and results were always repeated at least three times to check the reproducibility.

Polarization measurements performed at potentials in the range from -450 mV to -150 mV (SCE) at a scan rate of 0.33 mVs⁻¹. All measurements were carried out in aerated solution of 0.1 M of HCl in the absence and presence of different concentrations of inhibitors. The Tafel plots of the anodic and cathodic curves were extrapolated to obtain the corrosion potential (E_{corr}) and corrosion current density (i_{corr}).

Electrochemical impedance spectroscopy were performed at corrosion potentials, E_{corr} , over a frequency range of 10⁵ Hz to 0.5 Hz with a signal amplitude perturbation of 10 mV, using potentiostat/galvanostat (Gamry PCI 300/4) and personal computer with EIS300 software for calculations. Data were presented as Nyquist and Bode plots. Experiments were always repeated at least three times.

The electrochemical frequency modulation technique (EFM) provides a new tool for electrochemical corrosion monitoring. EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5 Hz was based on three arguments [31]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF2 and CF3 [32&33].

All electrochemical measurements were performed using Gamry Instrument (PCI 300/4) Potentiostat / Galvanostat /ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include DC105 software for potentiodynamic polarization measurements, EIS300 software for electrochemical impedance spectroscopy and EFM 140 software for electrochemical frequency modulation measurements along with a computer for collecting data. Echem Analyst 6.03 software was used for plotting, graphing, and fitting data.

III. RESULTS AND DISCUSSION

a) Potentiodynamic Polarization Measurements

Potentiodynamic polarization curves of copper electrode in 0.1 M HCl solution without and with various concentrations (100, 300, 500, 700, 900 ppm) of streptoquin and septazole at 25°C were recorded. The polarization curves of copper in 0.1 M HCl at 25°C in the presence and absence of different concentrations of streptoquin and septazole are shown in Figs.1 & 2. Electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic (β_a), cathodic (β_c) Tafel slopes and inhibition efficiency ($\eta\%$) were calculated and are listed in Table 2. The inhibition efficiency ($\eta\%$) and the corrosion rate (R_{corr}) were calculated using Eqs.1&2:

$$\eta (\%) = (i_{\text{corr}} - i_{\text{corr, (inh.)}} / i_{\text{corr}}) \times 100 \quad (1)$$

$$R_{\text{corr}} (\text{mm/year}) = 3270 \times (i_{\text{corr}} \times \text{EW/D}) \quad (2)$$

where i_{corr} is the corrosion current density (A cm⁻²), EW the equivalent weight of copper (g) and D the density of Cu (g cm⁻³).

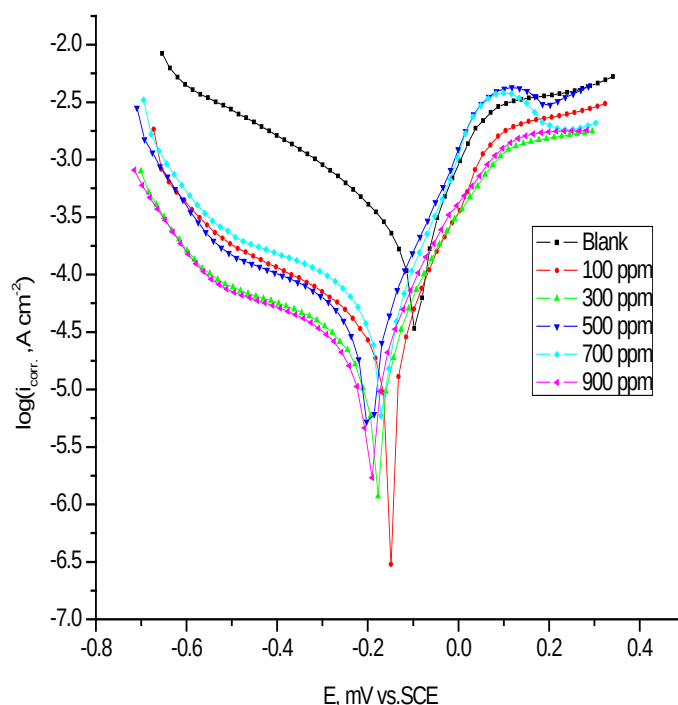


Figure 1 : Potentiodynamic polarization curves of copper in 0.1 M HCl at different concentrations of streptoquin at 25°C

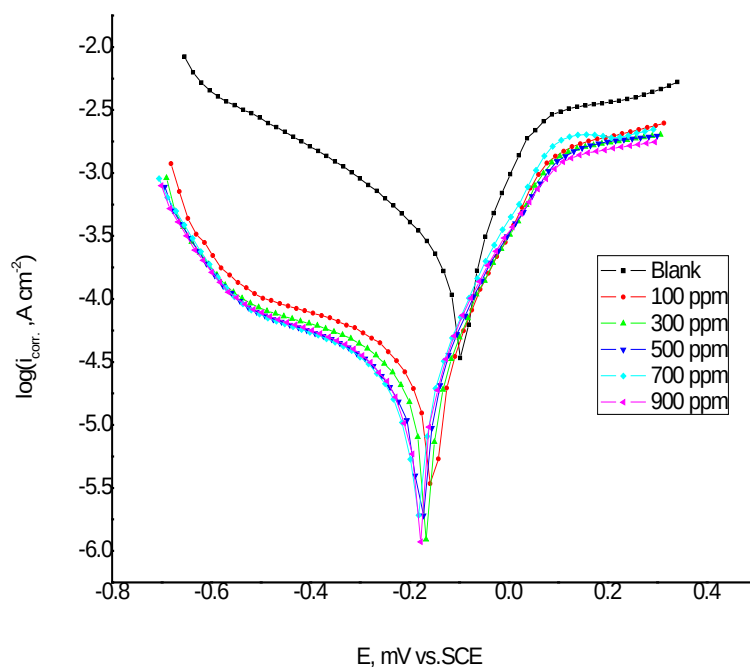


Figure 2 : Potentiodynamic polarization curves of copper in 0.1 M HCl at different concentrations of septazole at 25°C

The presence of increasing amounts of septazole and streptoquin led to a decrease in both the cathodic and anodic current density. It is clear from these data that the inhibitors may affect either the anodic or the cathodic reaction, or both [34]. Since the

anodic (β_a) and cathodic (β_c) Tafel slopes of streptoquin and septazole were found to change slightly with inhibitor concentration, this indicates that these inhibitors affected both of these reactions i.e. these drugs act as mixed type inhibitors [35].

Table 3 : Electrochemical parameters obtained from potentiodynamic polarization measurements of copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin and septazole at 25°C

Comp	Conc. Ppm	$-E_{\text{corr}}$ mV vs SCE	i_{corr} $\mu\text{A cm}^{-2}$	β_c mV dec ⁻¹	β_a mV dec ⁻¹	R_p Ohm cm ²	θ	$\eta\%$	R_{corr} mmy ⁻¹
Streptoquin	Blank	144	284.10	670	351	352	----	----	3.294
	100	154	101.80	650	258	786	0.642	64.2	1.181
	300	180	77.68	708	258	1058	0.727	72.7	0.901
	500	195	61.63	639	234	1206	0.783	78.3	0.715
	700	215	54.29	568	231	1313	0.809	80.9	0.630
	900	212	47.93	501	233	1442	0.831	83.1	0.556
Septazole	100	153	53.84	985	247	1590	0.813	81.3	0.624
	300	164	43.58	936	246	1942	0.847	84.7	0.505
	500	178	34.58	765	237	2296	0.878	87.8	0.401
	700	187	32.55	713	232	2362	0.886	88.6	0.378
	900	197	24.66	566	225	2840	0.913	91.3	0.286

The addition of streptoquin and septazole shift the E_{corr} values towards the negative. A compound can be classified as an anodic-or cathodic-type inhibitor when the change in E_{corr} value is larger than 85 mV [36]. Since the largest displacement exhibited by streptoquin and septazole was about 71 mV as shown in Table 3, it may be concluded that these molecules should considered as a mixed-type inhibitor, meaning that the addition of these drugs to 0.1 M HCl solution both reduces the anodic dissolution of copper and also retards the cathodic hydrogen evolution reactions. From the calculated values of ($\eta\%$) as shown in Table 3, the order of decreasing inhibition efficiency is as follows: streptoquin > septazole.

b) Effect of Temperature

From Table 4 we found that the corrosion rate increases with the rise of temperature and the inhibition

efficiency decreases with increasing temperature. This can be attributed to the shift of the adsorption-desorption equilibrium towards desorption. Such behaviour suggests that investigated compounds were physically adsorbed on copper surface. The activation energy (E_a^*) of the corrosion process was calculated using Arrhenius eq. (3):

$$i_{\text{corr}} = A \exp (-E_a^*/RT) \quad (3)$$

Where A is Arrhenius constant, R is the gas constant and T is the absolute temperature. Figures (3&4) show the Arrhenius plot ($\log i_{\text{corr}}$ vs. $1/T$) in the presence and absence of streptoquin and septazole. The values of activation energies E_a^* can be obtained from the slopes of the straight lines and are given in Table (5).

Table 4 : Electrochemical parameters obtained from potentiodynamic polarization measurements of copper in 0.1 M HCl in presence of 500 ppm from streptoquin and septazole at different temperature

Comp	TempK	$-E_{\text{corr}}$ mV vs SCE	i_{corr} $\mu\text{A cm}^{-2}$	β_c mV dec ⁻¹	β_a mV dec ⁻¹	R_p Ohm cm ²	θ	$\eta\%$	R_{corr} mmy ⁻¹
Streptoquin	308	173	99.16	578	269	803	0.736	73.6	1.150
Septazole		119	58.16	516	217	1140	0.846	84.6	0.675
Streptoquin	318	148	128.6	600	239	577	0.671	67.1	1.491
Septazole		166	103.1	606	252	749	0.736	73.6	1.196
Streptoquin	328	182	154.00	499	151	517	0.636	63.6	1.786
Septazole		165	127.00	430	185	579	0.700	70.0	1.473

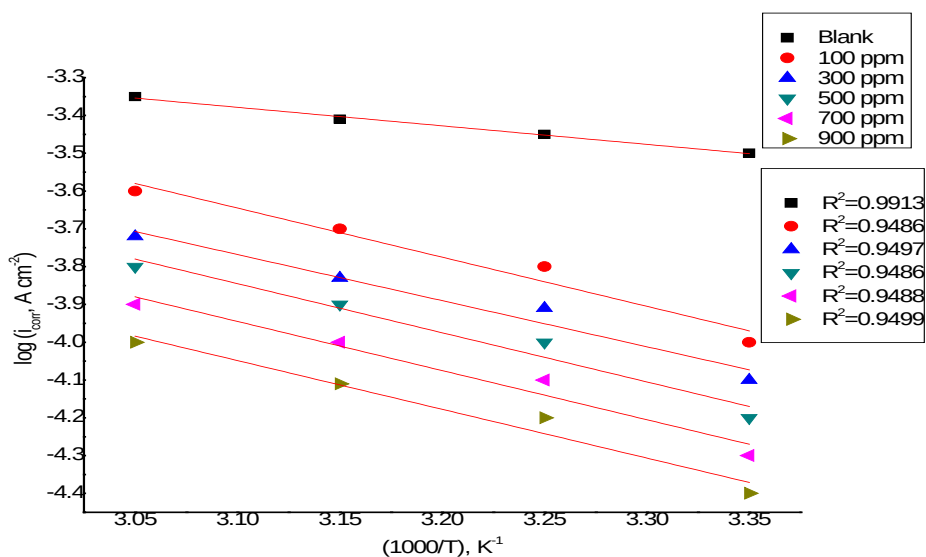


Figure 3 : Log i_{corr} vs. $(1/T)$ curves for the corrosion of copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin at different temperatures

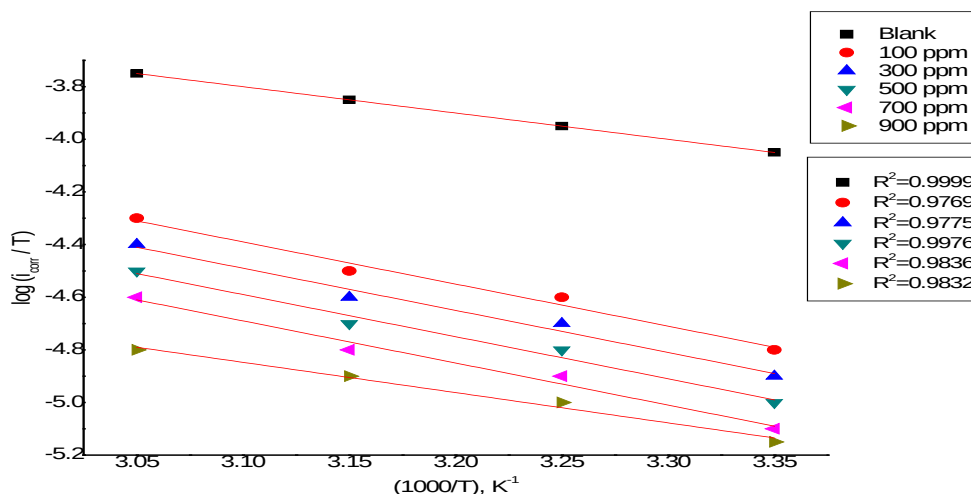


Figure 4 : $\log(i_{\text{corr}}/T)$ vs. $(1/T)$ curves for the corrosion of copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin at different temperatures

It is noted that the values of activation energy is higher in the presence of drugs than in their absence indicating that inhibitors exhibit low $\eta\%$ at elevated temperatures [37] and also, due to the film formation on copper surface. An alternative formulation of the Arrhenius equation is the transition state equation [38]:

$$i_{\text{corr}} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (4)$$

where h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Figures 5&6) show a plot of $\log(i_{\text{corr}}/T)$ vs. $(1/T)$. Straight lines were obtained with slopes

of $(\Delta H^*/2.303R)$ and intercepts of $(\log R/Nh + \Delta S^*/2.303R)$

Table 5 : Kinetic-thermodynamic corrosion parameters for copper corrosion in the absence and presence of various concentrations of streptoquin and septazole

Inhibitors	Conc. ppm	E_a^* kJ mol ⁻¹	$-\Delta H^*$ kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹
Streptoquin	Blank	9.40	19.1	226.3
	100	23.4	22.1	209.7
	300	24.7	23.9	205.5
	500	25.1	24.7	203.6
	700	25.3	25.7	201.7
	900	25.7	26.6	200.4
Septazole	100	37.9	22.9	192.4
	300	38.3	24.9	190.5
	500	39.1	26.8	188.6
	700	40.2	28.7	186.7
	900	40.8	30.6	184.7

The values of ΔH^* and ΔS^* were calculated and listed in Table (5). The negative values of ΔH^* reflect that the process of corrosion is an exothermic one. The negative values of ΔS^* implies that the activation complex is the rate determining step that represents an association rather than dissociation step [39]. This means that the activated molecules are in higher order state than that the initial state.

c) Adsorption Isotherm

In order to get a better understanding of the electrochemical process on the metal surface, adsorption was studied. For determining the related mechanism, adsorption isotherms were drawn. A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experimental data of the present work. The simplest equation is that due to [40] Langmuir which is given by the general relation:

$$C/\theta = 1/K_{ads} + C \quad (5)$$

where K_{ads} is the equilibrium constant for the adsorption/desorption process, C is the inhibitor concentration in the bulk of the solution in mol L⁻¹. From the intercepts of the straight lines on the C/θ axis, one can calculate K_{ads} values that relate the standard free energy of adsorption, (ΔG_{ads}°), as given by this Eq. [41]:

$$K_{ads} = 1/55.5 \exp (-\Delta G_{ads}^\circ / RT) \quad (6)$$

The value of 55.5 is the concentration of water in the bulk solution in mol L⁻¹. Free energy, ΔG_{ads}° , values were calculated and are given in Table (6), the negative values of ΔG_{ads}° indicate spontaneous adsorption of inhibitors on copper surface [42]. Generally, values of ΔG_{ads}° up to -20 kJ mol⁻¹ are

consistent with physisorption, while those around -40 kJ mol⁻¹ or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from inhibitor molecules to the metal surface to form co-ordinate bond [43]. the calculated ΔG_{ads}° values are 22-36 kJ mol⁻¹ indicating that the adsorption mechanism of septazole and streptoquin in 0.1 M HCl solution at the studied temperatures is mixed one (physisorption and chemisorption). Figs. (7&8) show that the plot of C/θ vs. C for streptoquin and septazole are linear plots which obtained for the different temperatures and inhibitors, indicating that the adsorption of these compounds followed Langmuir adsorption isotherms. The various adsorption parameters obtained from this isotherm are listed in Table (6).

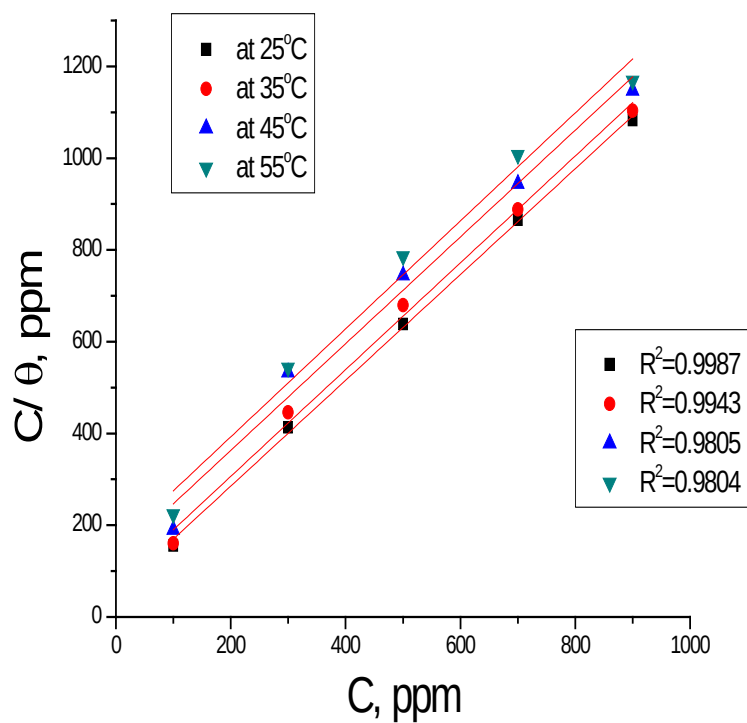


Figure 7 : The linear form of Langmuir adsorption isotherm of streptokinase on copper surface in 0.1 M HCl solution

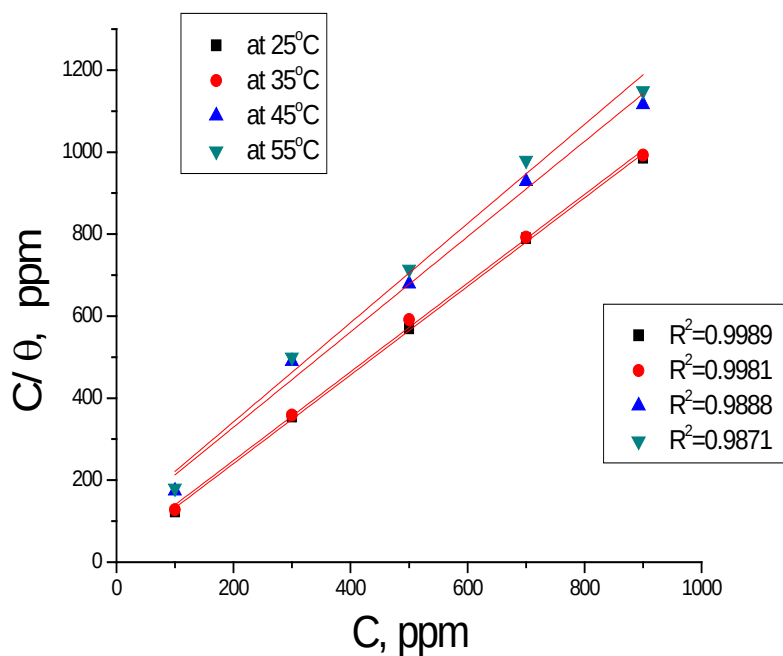


Figure 8 : The linear form of Langmuir adsorption isotherm of septazole on copper surface in 0.1 M HCl solution

Thermodynamic adsorption parameters such as enthalpy of adsorption $\Delta H_{\text{ads}}^{\circ}$ and entropy of adsorption $\Delta S_{\text{ads}}^{\circ}$ can be deduced from integrated version of the Vant't Hoff equation expressed by [44]:

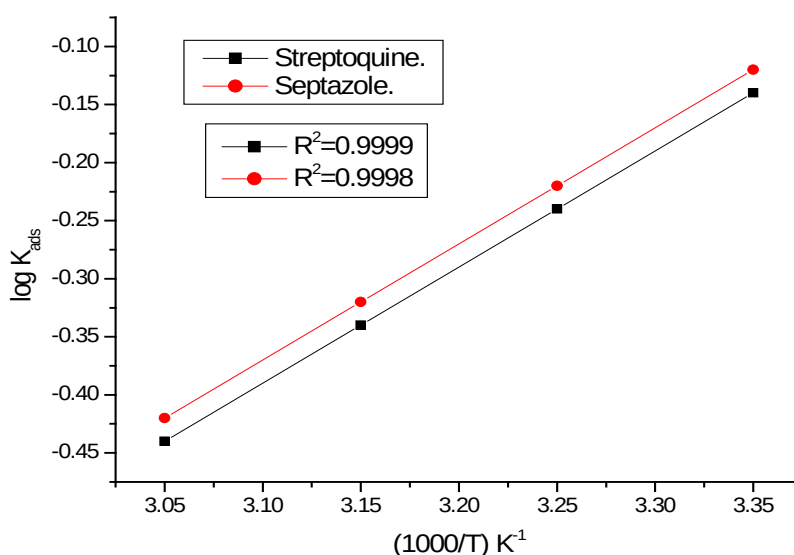
Table 6 : Thermodynamic parameters for the adsorption of streptoquin and septazole on copper in 0.1 M HCl at different temperature

Inhibitors	Temp., K	$K_{ads} \times 10^{-4} M^{-1}$	$-\Delta G_{ads}^{\circ}$ kJ mol ⁻¹	$-\Delta H_{ads}^{\circ}$ kJ mol ⁻¹	$-\Delta S_{ads}^{\circ}$ J mol ⁻¹ K ⁻¹
Streptoquin	298	0.72	30.7	31.2	107.6
	308	0.53	28.1		
	318	0.30	23.4		
	328	0.25	21.9		
Septazole	298	1.44	36.4	45.0	147.6
	308	1.11	34.3		
	318	0.36	24.9		
	328	0.35	24.4		

$$\ln K_{ads} = (-\Delta H_{ads}^{\circ}/RT) + (\Delta S_{ads}^{\circ}/R) + \ln(1/55.5) \quad (7)$$

Figure 9 shows the plot of $\ln K_{ads}$ Vs. $1/T$ which gives straight lines with slopes $(-\Delta H_{ads}^{\circ}/2.303R)$ and

intercepts $[(\Delta S_{ads}^{\circ}/2.303R) + \ln(1/55.5)]$. Calculated values of ΔH_{ads}° and ΔS_{ads}° using the Van't Hoff equation are listed in Table 6.

**Figure 9 :** Log K_{ads} vs. $(1/T)$ curves for the corrosion of copper in 0.1 M HCl in the absence and presence of different concentrations of septazole and streptoquin at different temperatures

Negative sign of ΔH_{ads}° indicates that the adsorption of septazole and streptoquin on copper surface is an exothermic process. ΔH_{ads}° is about 31.2-45 kJ mol⁻¹ which is larger than the common physical adsorption heat (40 kJ mol⁻¹), but smaller than the common chemical adsorption heat (100 kJ mol⁻¹) [45], probably meaning that both physical and chemical adsorption take place (i.e. comprehensive adsorption). The negative ΔS_{ads}° values are accompanied with

exothermic adsorption process. This is agrees with the expected, when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [46].

d) Electrochemical Impedance Spectroscopy

Electrochemical impedance is a powerful tool in the investigation of the corrosion and adsorption phenomena [47]. The correlation of the experimental

impedance plot to an equivalent circuit enables the verification of the mechanistic model for the system. Such a correlation leads to the calculation of the numerical values corresponding to physical and/or chemical properties of the electrochemical system [48, 49]. The impedance data of Cu, recorded after 30 min immersion in 0.1 M HCl are presented as Nyquist and Bode plots in presence and absence of various concentrations of streptoquin and septazole are shown in Figures (10&11), respectively. The Nyquist plots show

a single semi-circle shifted along the real impedance (Z_r) axis, single capacitive loop, which is attributed to charge transfer of the corrosion process, and the diameters of the loops increase with the increase in the concentration of the drugs. The Bode plots show resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region (horizontal line and a phase angle = 0) at low frequencies. These plots show two overlapped phase maxima at intermediate and low frequencies.

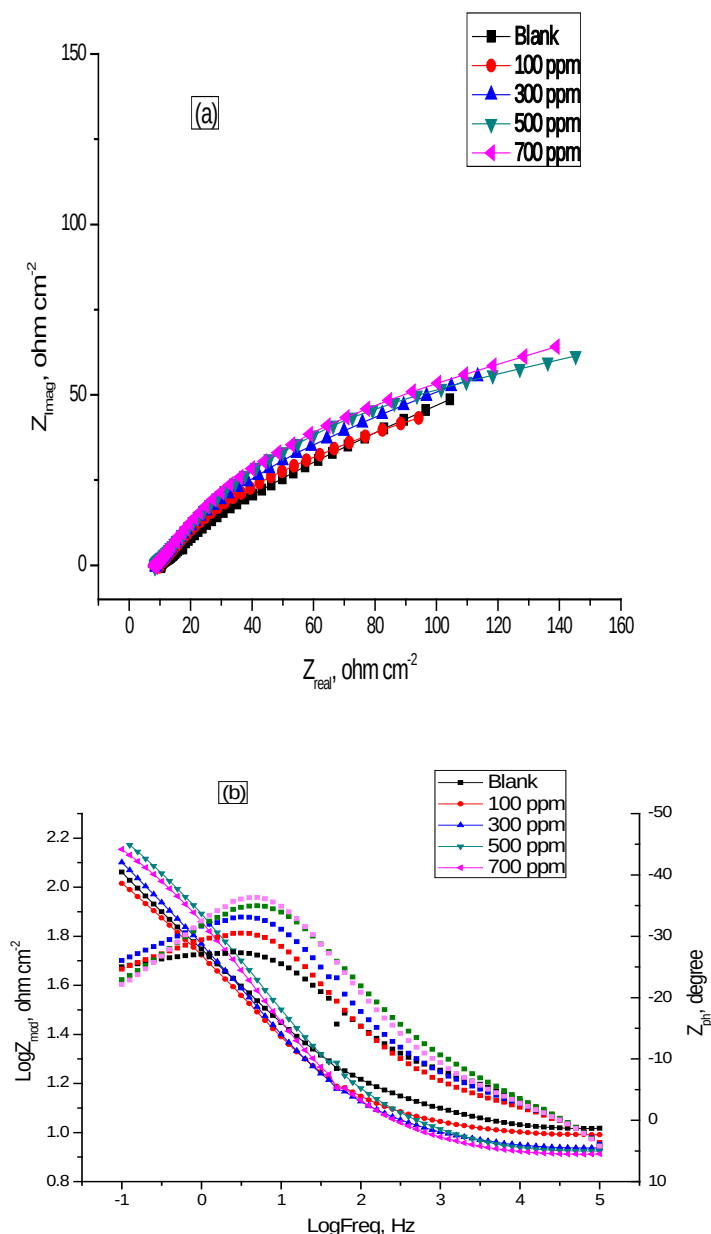


Figure 10 : The Nyquist (a) and Bode (b) plots for corrosion of copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin

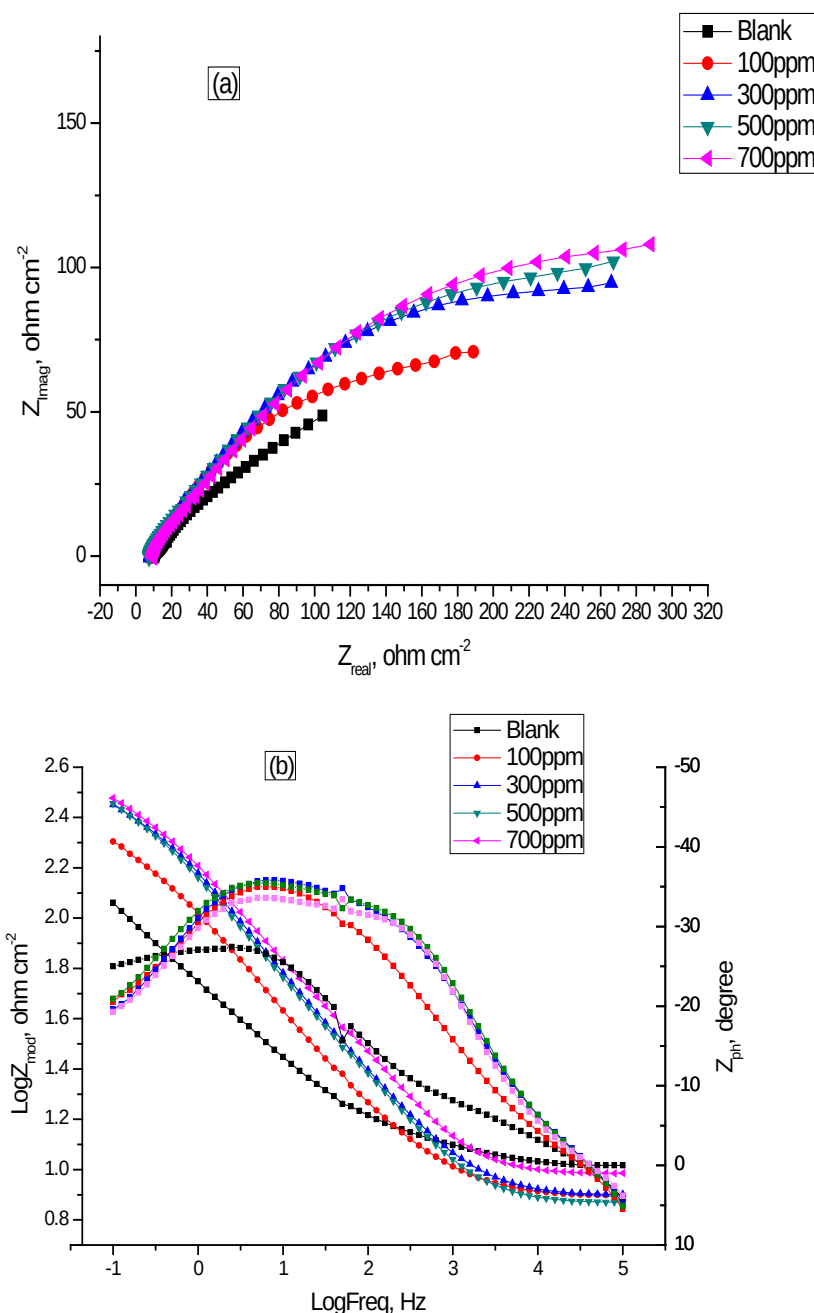


Figure 11 : The Nyquist (a) and Bode (b) plots for corrosion of copper in 0.1 M HCl in the absence and presence of different concentrations of septazole

The impedance data of the copper electrode in the presence of different inhibitors concentrations were analyzed using the equivalent circuit shown in Figure 12. This circuit includes constant phase elements (CPE) in place of capacitors to represent various types of non homogeneities typical of corroding electrodes such as surface roughness, insufficient polishing, grain boundaries and surface impurities [50]. The impedance of this element is frequency dependent, and can be mathematically expressed using two parameters, Y_0 and n as:

$$Z_{CPE} = Y_0^{-1} (j \omega)^{n-1} \quad (8)$$

where Y_0 is the CPE coefficient, ω the angular frequency ($\omega = 2\pi f$, where f is the AC frequency). According to the value of n , Eq. (8) accounts for an inductance ($n = -1$), a resistance ($n = 0$), a Warburg impedance ($n = 0.5$) or a capacitance ($n = 1$). A Warburg element

occurs when charge carriers diffuse through a material. A rough or porous surface can cause a double layer capacitance to appear as a constant phase element with n varying between 0.5 and 1. This circuit is typical of oxide-coated metals and has been used before by other authors in relation to copper corrosion in potable water [51]. R_s represents the solution resistance between the electrode surface and the tip of the Luggin capillary, Z_{CPEo} a constant related to the surface oxide, R_o the resistance to current flow through defects in the surface oxide, Z_{CPEdl} a constant related to the double layer and R_{dl} the double layer resistance. From these Nyquist plots, the difference in real impedance at lower and higher frequencies is generally considered as charge-transfer resistance. The resistances between the metal and outer Helmholtz plane (OHP) must be equal to the R_{ct} . The adsorption of inhibitor molecules on the metal surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the metal surface. This modification results in an increase of charge-transfer resistance. The R_{ct} values increased with inhibitors concentrations may suggest the formation of a protective layer on the copper surface. This layer makes a barrier for mass and charge-transfer. The values of the charge-transfer resistance (R_{ct}) were obtained from the difference in real component (Z') of impedance at lower frequencies. Also the double layer capacitances (C_{dl}) were calculated by the Eq. (9) [31].

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \quad (9)$$

where f_{max} is the frequency value at which the imaginary component (Z'') of impedance is maximum. The calculated values of R_{ct} and C_{dl} are listed in Tables (7). The data obtained from fitted spectra are listed in Table 7. The degree of surface coverage (θ) and $\eta\%$ were calculated from the EIS data using following equation:

$$\eta\% = \theta \times 100 = [1 - (R_{ct}^*/R_{ct})] \times 100 \quad (10)$$

where R_{ct} and R_{ct}^* are the charge-transfer resistances with and without the inhibitors, respectively. θ and η are also listed in Table 7, and also show that the R_s values are very small compared to the R_{ct} values. By increasing the inhibitor concentrations, the R_{ct} values increase and the calculated C_{dl} values decrease, which causes an increase of θ and $\eta\%$, the R_{ct} are obtained by septazole at all concentrations is higher than that obtained by streptoquin. The order of the IE obtained from the R_{ct} values is: septazole > streptoquin.

As it can be seen from Tables 7, the C_{dl} values tend to decrease with the increase of the concentration of the surfactants in 0.1 M HCl solution. The decrease in the C_{dl} , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that surfactants molecules function by adsorption at the metal/solution

interface. The inhibition efficiencies calculated from impedance data are closed to those obtained from potentiodynamic polarization measurements. The results show the good agreement between measurements obtained from both techniques.

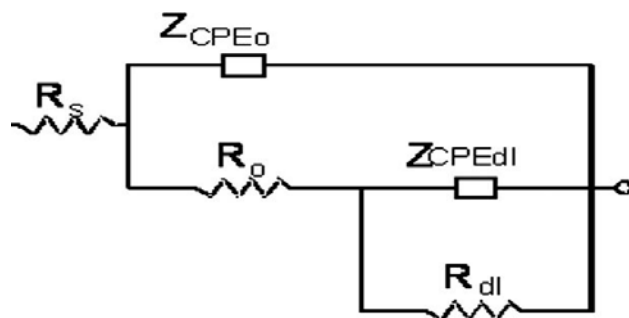


Figure 12: Equivalent circuit proposed to fit the experimental data when two time constants are present

Table 7: Electrochemical kinetic parameters obtained by EIS technique for copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin and septazole

Comp.	Conc. ppm	R_p ohm cm^2	C_{dl} $\mu F cm^{-2}$	θ	$\eta\%$
Streptoquin	Blank	172.7	2640	----	----
	100	193.4	1079	0.107	10.7
	300	246.4	1013	0.299	29.9
	500	268.0	633	0.359	35.9
	700	269.4	520	0.366	36.6
Septazole	100	304.1	1980	0.432	43.2
	300	418.8	1910	0.588	58.8
	500	447.4	1590	0.614	61.4
	700	491.9	1560	0.649	64.9

e) Electrochemical Frequency Modulation (EFM)

Electrochemical frequency modulation (EFM) technique is a new tool for monitoring the electrochemical corrosion. EFM is non-destructive technique, rapid test, gives directly values of the corrosion current without a prior knowledge of Tafel constants and has also great strength due to the causality factor, which serve as an internal check on the validity of the EFM measurements Table 8 shows the corrosion kinetic parameters such as inhibition efficiency ($E_{EFM}\%$), corrosion current density ($\mu A cm^{-2}$), Tafel constants (β_a & β_c) and causality factors (CF-2, CF-3) at different concentrations of drugs at 25°C. Figures 13-15 represent the EFM intermodulation spectra of copper in 0.1 M HCl devoid of and containing 500 ppm concentrations of streptoquin and septazole, respectively. The inhibition efficiency, $E_{EFM}\%$ of streptoquin and septazole was calculated using eq. (1). As can be seen from Table 8, the corrosion current densities decrease with increase in streptoquin and

septazole concentrations. The causality factors indicate that the measured data are of good quality. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0 then it can be deduced that the measurements are influenced by noise. If the causality factors are approximately the predicted values of 2.0

and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [32]. The calculated inhibition efficiency $E_{\text{EFM}} \%$ enhances with increasing streptoquin and septazole concentration.

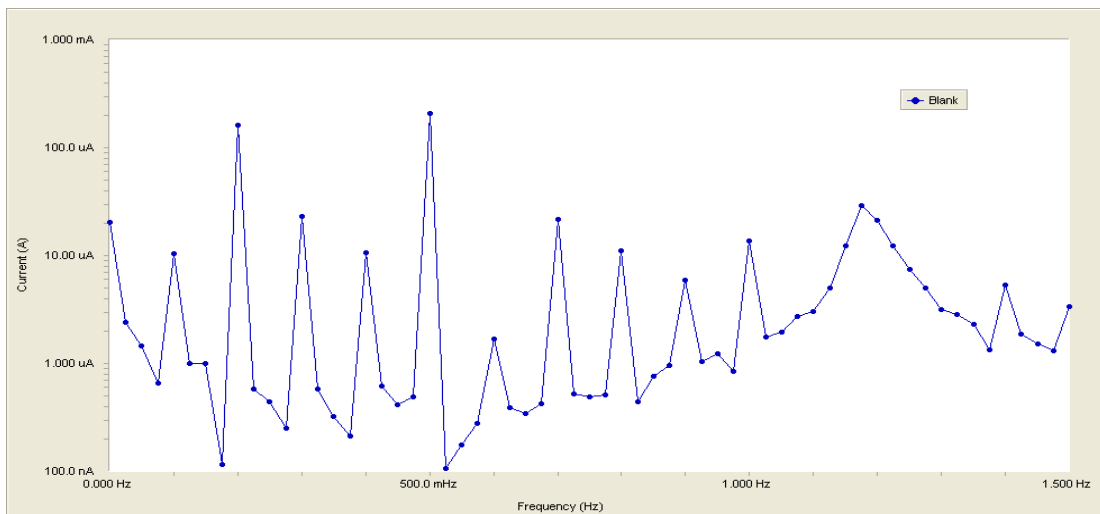


Figure 13 : Intermodulation spectra recorded for copper electrode in 0.1 M HCl solutions

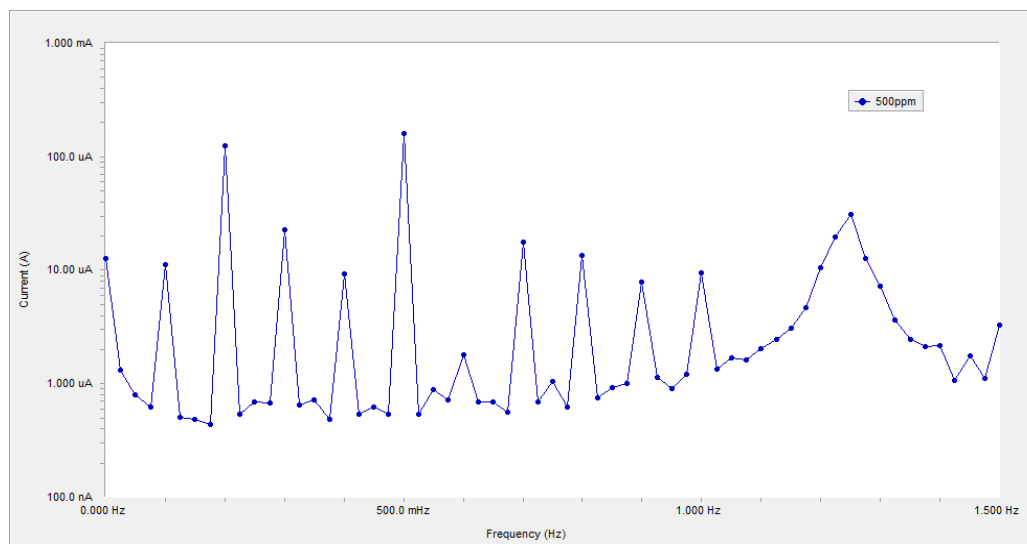


Figure 14 : Intermodulation spectra recorded for copper electrode in 0.1 M HCl solutions in the absence and presence 500 ppm of streptoquin

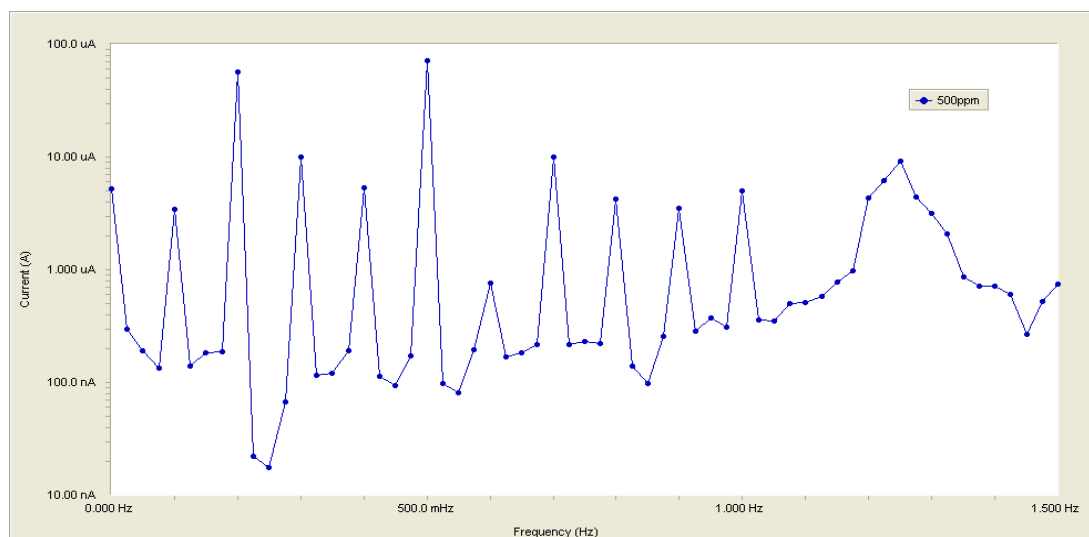


Figure 15 : Intermodulation spectra recorded for copper electrode in 0.1 M HCl solutions in the presence 500 ppm of septazole

Table 8 : Electrochemical kinetic parameters obtained from EFM technique for copper in 0.1 M HCl in the absence and presence of different concentrations of streptoquin and septazole

Comp.	Conc. ppm	i_{corr} $\mu A\ cm^{-2}$	β_a $mVdec^{-1}$	β_c $mVdec^{-1}$	$E_{EFM}\%$	CR mpy	CF-2	CF-3
Streptoquin	Blank	135.00	40	57	-----	34.66	1.828	3.845
	100	134.30	42	61	0.52	33.98	2.093	3.361
	300	122.30	37	50	9.4	32.00	1.997	3.781
	500	95.68	37	55	29.13	25.03	2.167	3.250
	700	77.35	28	39	42.70	20.23	1.908	3.938
Septazole	100	77.34	40	65	42.70	20.23	1.976	3.843
	300	57.55	36	59	57.40	12.64	2.001	3.644
	500	49.88	41	67	63.10	13.05	1.942	3.130
	700	48.31	45	81	64.21	15.05	2.062	3.308

f) Quantum Chemical Calculation

Over the past decades the semi empirical molecular orbital methods have been widely used in computational studies. Semi empirical methods serve as efficient computational tools which can yield fast quantitative estimates for a number of properties [52]. MNDO (modified neglect of differential overlap) is a semiempirical methods based on the NDDO (neglect of diatomic differential overlap) approximation. The quantum chemical calculations were employed to give further insight into the mechanism of inhibition action of streptoquin and septazole. For this purpose the highest occupied molecular orbital E_{HOMO} , energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO and Mulliken charges on charge we can observe the presence of excess of negative charge on nitrogen, oxygen and sulfur atoms can be adsorbed on the copper surface using these active centres leading to the corrosion inhibition action.

The calculated parameters such as E_{HOMO} , E_{LUMO} and the dipole moment (μ) of the two inhibitors were shown in Table 9, the dipole moment (μ) is an indicator of the electronic distribution in a 1 molecule and is one of the properties used to discuss and to rationalize the structure. Low value of the dipole moment (μ) will favour the accumulation of inhibitor molecules on the metallic surface. The comparison between the calculated dipole moments of inhibitors reveals that the lower septazole has better inhibition efficiency. E_{HOMO} often indicates the electron donating ability of the molecule and the inhibition efficiency increases with increasing E_{HOMO} values. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Increasing of the values of the E_{HOMO} facilitates adsorption (and therefore inhibition) by influencing on the transport process through the adsorbed layer. HOMO and LUMO electronic density distribution of

streptoquin and septazole were plotted in Figure 15. There is a general consensus by several authors that the more negatively charged heteroatom, the more it can be adsorbed on the metal surface through donor-acceptor type reaction [53]. From the values of Mulliken charge we can observe the presence of excess of negative charge on nitrogen, oxygen and sulphur atoms can be adsorbed on the copper surface using these active centres leading to the corrosion inhibition action. Table 9 shows the quantum chemical calculation parameters

(E_{HOMO} , E_{LUMO} , $\Delta E = (E_{\text{LUMO}} - E_{\text{HOMO}})$, dipole moment (μ), heat of formation and ionization potential) for streptoquin and septazole. From these tables the less negative E_{HOMO} and the smaller ΔE reflect a great inhibition efficiency of the inhibitors [54]. From the energy of highest occupied molecular orbital (E_{HOMO}), the order of inhibiting efficiency is as follow: septazole > streptoquin. This is a good agreement with the experimental data obtained by potentiodynamic polarization, EIS and EFM techniques.

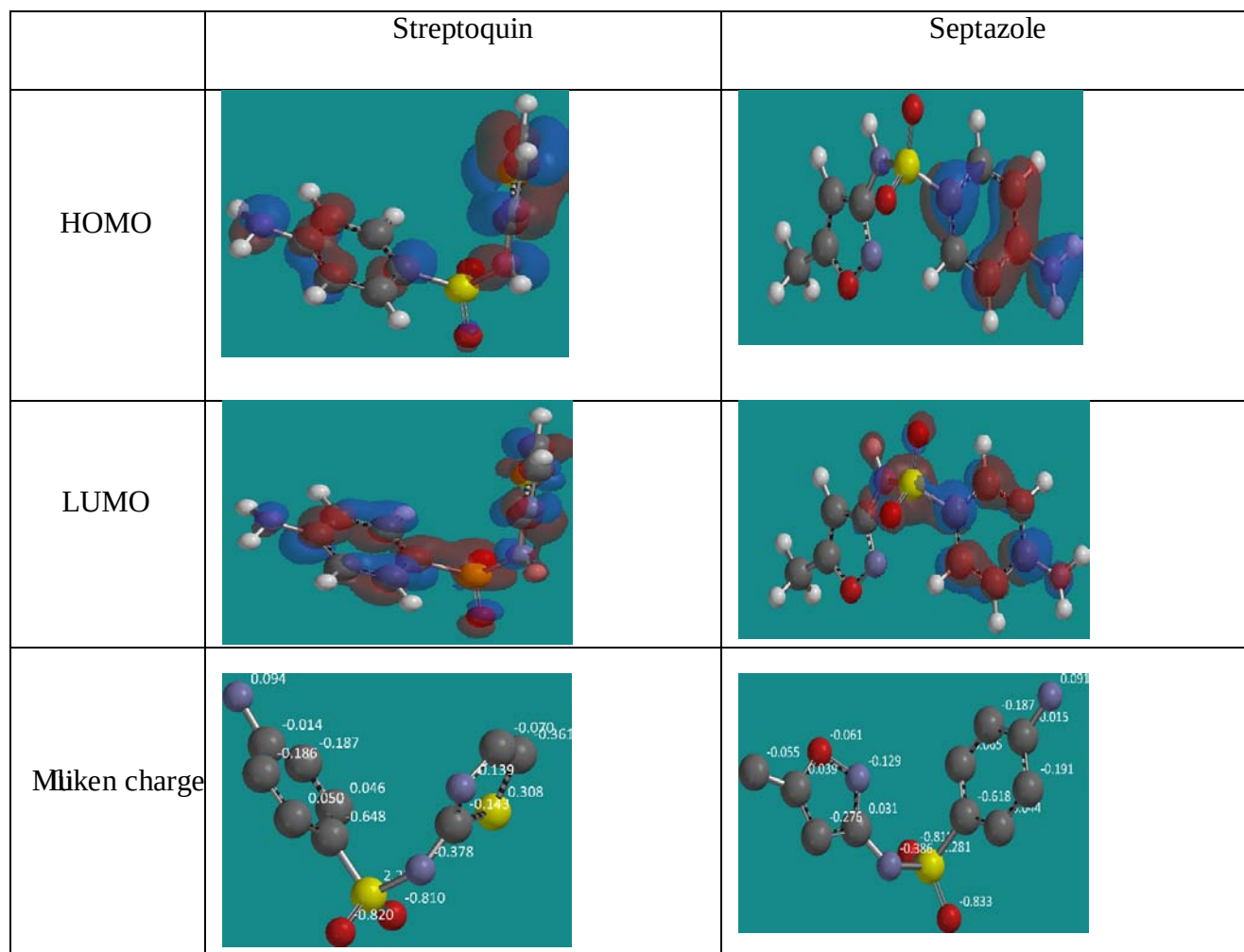


Figure 15 : Molecular orbital plots and Mulliken charge of streptoquin and septazole using MNDO

Table 9 : The calculated quantum chemical parameters of streptoquin and septazole

Parameters	streptoquin	Septazole
E_{HOMO} (ev)	-9.27	-9.19
E_{LUMO} (ev)	-0.71	-0.94
ΔE (ev)	8.56	8.25
Dipole moment (μ) (debye)	6.23	4.44
Surface area $\text{\AA}^2$	252.88	263.80

IV. CONCLUSIONS

The corrosion resistance of copper increases with the increasing concentration of streptoquin and septazole and decreases with increasing temperature indicating that the inhibition occurs through mainly physical adsorption of the investigated drugs on copper surface. These drugs act as mixed-type inhibitors, suppressing the corrosion reactions by forming a protective adsorption film on copper surface. Adsorption

of these inhibitors on copper surface obeys Langmuir isotherm. The increase in concentration of the investigated drugs leads to increase in the values of the charge transfer resistance (R_{ct}) and a decrease in the values of double layer capacitance (C_{dl}). The results obtained using these different techniques were in good agreement verifying the validity of data obtained by these techniques. Comparison of quantum chemical calculations and experimental data exhibit good correlation confirming the reliability of the methods employed here.

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