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The Inhibition Effect of Cefotaxime Drug Towards The Corrosion of Copper in Acidic Solutions

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ABSTRACT

In this research, the use of cefotaxime as corrosion inhibitor for copper in nitric acid solution has been performed through weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The effect of inhibitor concentration, temperature and immersion time against inhibitor action was investigated. Results show that cefotaxime may be used as an efficient inhibitor for copper in nitric acid solutions. Potentiodynamic polarization studies reveal that cefotaxime acts as a mixed-type inhibitor without any change in the mechanism of hydrogen evolution. The adsorption of this compound on copper surface obeys Langmuir's adsorption isotherm and has a physiosorption mechanism.

الملخص

في هذا البحث تم دراسة إستخدام دواء cefotaxime **كمثبط لتآكل النحاس في محلول حامض النيتريك بإستخدام طريقة الفقد في الوزن و** potentiodynamic polarization **و** electrochemical impedance spectroscopy **حيث درس تأثير كلا من : تركيز** cefotaxime **و درجة الحراره و زمن الغمر علي عملية تثبيط تآكل النحاس وقد أظهرت النتائج أن** cefotaxime **يمكن إستخدامه كمثبط كفؤ لعملية تآكل النحاس في محاليل حامض النيتريك حيث أن** كفاءة التثبيط تزداد بزيادة تركيز **المثبط** و تقل بزيادة درجة الحراره و أن عملية إدمصاص **المثبط** علي سطح السبيكه هي عمليه طارده للحراره و تلقائيه **كما أظهرت النتائج أن عملية إمتزاز مركب المثبط هي عملية فيزيائية تتبع** Langmuir's adsorption isotherm.

1.INTRODUCTION

Copper and its alloys, because of their excellent resistance to corrosion in neutral aggressive media and their ease of processing, they are widely used in industries(1), especially in electronics, solar cell fittings, household products, structural engineering, art and decoration, coinage and biomedical application. Roughly, 19% of the weight of a mobile phone nowadays consists of copper and copper alloys. Even though copper is corrosion resistant due to its natural oxide film, it is prone to corrode in solutions that contain oxygen and high concentration of chloride, sulphate, sulphide and nitrate ions. A variety of potentially damaging environments require versatile inhibition actions. Although an inhibitor is sometimes added to avoid tarnishing, in the majority of cases the inhibitor's purpose is to prevent or postpone corrosion attack. Numerous investigations have been conducted on the corrosion inhibition of copper and its alloys (2–10). HNO_3 is an oxidizing acid and its oxidizing capacity depends on its concentration(11-13). Metals react with nitric acid by giving hydrogen and the metal nitrates. The evolved hydrogen is used up in reducing nitric acid to various products (14). It is known (15)that most of the brasses metals react with nitric acid to form hydrogen rich compounds (NH_3 or NH_2OH), whereas noble metals like silver or copper produce compounds rich in oxygen (NO_2, NO and HNO_2).

It is noticed that presence of hetero-atom such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. Amongst these organic compounds and their derivatives such as azoles (16, 17), amino acids (18) and many others, but these compounds are highly toxic. Recently, researches are oriented to the development of green corrosion inhibitors, compounds with good inhibition efficiency but low risk of environmental pollution (19). Antibiotic drugs have attracted attention in the field of corrosion inhibition for many decades. As natural products, they are a source of non-toxic, eco-friendly, readily available and renewable inhibitors for preventing metal corrosion (20, 21). So our aim is to study the inhibiting effect of cefotaxime on copper corrosion in nitric acid solution using chemical and electrochemical techniques.

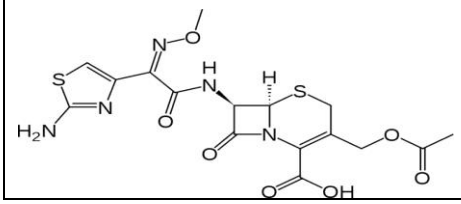
2.EXPERIMENTAL

2.1.Materials and solutions

Experiments were performed using copper specimens (99.98%) were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and copper electrode. The aggressive solution used was prepared by dilution of analytical reagent grade 70% HNO_3 with bidistilled water. Cefotaxime was obtained from Glaxo SmithKline, Medical Union Pharmaceuticals, Alexandria Co.

for Pharmaceuticals Egypt. The stock solution (1x 10^{-3}M) of cefotaxime was used to prepare the desired concentrations by dilution with bidistilled water. The concentration range of cefotaxime used was (0.5x 10^{-4} - 8x10^{-4} M). Its chemical structure is shown in Table(1).

Table1. Chemical structure of cefotaxime .

Structure	Mol. formula	Mol.wt.
	$C_{16}H_{17}N_5O_7S_2$	455.465g/mol

2.2.Weight loss measurements

The weight loss measurements were carried out in a 100 ml glass beaker placed in a thermostat water bath. The solution volume was 100 ml. The used copper coupons had a square form (length = 2 cm, width = 2 cm, thickness = 0.2 cm). The coupons were weighed and suspended in 100 ml of an aerated 1 M HNO_3 solution with and without different concentrations of cefotaxime for 3 h exposure period of time at (25 -45) ± 1 ºC. At the end of the tests, the coupons were taken out, washed with bi-distilled water, degreased with acetone, washed again with bi-distilled water, dried, and then weighed using an analytical balance. The inhibition efficiency (% IE) over the exposure time period were calculated according to the following equation(12):

$$\%\, IE = \theta \times 100 = \left(1 - \frac{W_{(inh)}}{W_{(free)}}\right) \times 100 \qquad (1)$$

where, θ surface coverage, $W_{(free)}$ and $W_{(inh)}$ are the weight loss in the absence and presence of inhibitor, respectively.

2.3. Electrochemical measurements

Electrochemical measurements were performed in three-electrode glass cell at constant temperature of 25 ± 1 ºC, a platinum electrode was used as counter electrode, and saturated calomel electrode (SCE) was used as reference electrode. The working electrode was embedded in epoxy resin, leaving a geometrical surface area of 1 cm^2 exposed to the electrolyte. Potentiodynamic (Tafel) polarization curves and electrochemical impedance measurements were carried out using a computer controlled Gamry Instrument PCI4-G750 Potentiostat/Galvanostat/ZRA.

This includes a Gamry Framework system based on the ESA400, Gamry applications that include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.
Accordingly all experiments were carried out after 30 minute immersion of metal specimens into the electrolyte. Tafel polarization curves were obtained using a sweep rate of 1 mV s^{-1} in the potential range from -1000 mV to 1200mV with respect to the open circuit potential. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The corrosion current densities(i_{corr}) was used for the calculation of inhibition efficiency and surface coverage (θ) as below (22):

$$\%\,IE = \theta \times 100 = \left(1 - \frac{i_{corr(inh)}}{i_{corr(free)}}\right) \times 100 \qquad (2)$$

Where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.
Electrochemical impedance spectra were obtained in the frequency range of 0.1 Hz to 100 kHz with perturbation amplitude of 5 mV at the corrosion potential. The efficiency of the inhibition and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations(21,22):

$$\%\,IE = \theta \times 100 = \left(1 - \left[\frac{R^{\circ}_{ct}}{R_{ct}}\right]\right) \times 100 \qquad (3)$$

Where R^{o}_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively.

3.RESULTS AND DISCUSSION

3.1.Weight loss measurements

Figure (1) show the weight loss-time curves for copper in 1M nitric acid in the presence and absence of different concentrations of cefotaxime at 25 ºC. These curves are characterized by a sharp rise in weight loss from the beginning. Curves for additives containing system fall below that of the free acid. These curves indicated that, the weight loss of copper depends on the concentration of this additive. Increase in bulk concentration and consequently increase of surface coverage by the additive increases their inhibition efficiencies towards copper dissolution. As shown in Table (2) the inhibition efficiency of cefotaxime increases with the increase of their concentrations in the corrosive medium. It is thus obvious that increase of bulk concentration and consequently, increase of surface area coverage by the additive retards the dissolution copper.

The inhibitory behavior of this compound against copper corrosion can be attributed to the adsorption of cefotaxime on the copper surface, which limits the

dissolution of the latter by blocking of its corrosion sites and hence decreasing the corrosion rate, with increasing efficiency as their concentrations increase. Cefotaxime can be adsorbed by the interaction between the lone pairs of electrons of the nitrogen, sulphur and oxygen atoms with the copper surface. This process is facilitated by the presence of low lying d orbitals in the copper ions. Recently it was found that the formation of donor–acceptor surface complexes between free electrons of an inhibitor and a vacant d orbital of a metal is responsible for the inhibition of the corrosion process (23).

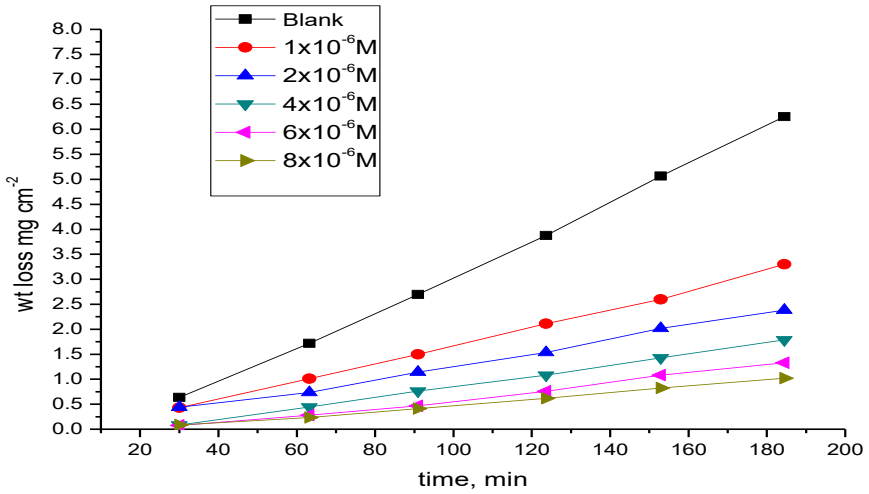


Figure 1. Weight loss-time curves for the corrosion of copper in 1 M HNO_3 in the absence and presence of different concentrations of cefotaxime at 25 ±1°C.

Table 2. Corrosion rate (C.R.) in (mg cm^{-2} min^{-1}) and inhibition efficiency data obtained from weight loss measurements for copper in 1 M HNO_3 solutions without and with various concentrations of cefotaxime at 25 ± 1°C.

Conc.,M	C.R., mg cm^{-2} min^{-1}	θ	% IE
1 M HNO_3	0.531	-	-
$0.5x10^{-4}$M	0.271	0.589	58.9
$2x10^{-4}$M	0.235	0.726	72.6
$4x10^{-4}$M	0.174	0.777	77.7
$6x10^{-4}$M	0.132	0.864	86.4
$8x10^{-4}$M	0.072	0.889	88.9

3.1.2. Effect of temperature and activation Parameters of Corrosion Process

The dissolution of copper in 1 M HNO_3 acid increases by increasing temperatures, the dissolution of copper in 1 M HNO_3 in the presence of cefotaxime at $1x10^{-6}$ - $8x10^{-6}$M was studied by weight loss method over a temperature range 25-45^{o}C. The Corrosion rate of copper dissolution increases as the temperature increases, but at lower rate than in uninhibited solutions as shown in Table (3). The inhibition efficiency of the additives decreases with rising the temperature which proves that the adsorption of these compounds on the surface of copper occurs through physical adsorption of the additives on the metal surface. Desorption is aided by increasing the reaction temperature.

The apparent activation energy (Ea*), the enthalpy of activation (ΔH*) and the entropy of activation (ΔS*) for the corrosion of copper and brass in 1 M HNO_3 solution in the absence and presence of different concentrations of cefotaxime were calculated from Arrhenius-type equation:

$$Rate(k) = A\, e^{\frac{-E_a^*}{RT}} \qquad (4)$$

and transition-state equation(24):

$$Rate(k) = \frac{RT}{Nh}\, e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \qquad (5)$$

Where (A) is the frequency factor, (h) is the Planck's constant, (N) is Avogadro's number and (R) is the universal gas constant.

Kinetic parameters obtained from plots of log Rate vs. (1/T)[Figure(2)] and log (Rate/T) vs. (1/T) [Figure (3)] are given in Table (4). Inspection of Table (4) shows that higher values were obtained for (Ea*) and (ΔH*) in the presence of inhibitor indicating the higher protection efficiency observed for this inhibitor. There is also a parallism between increases in inhibition efficiency and increases in (Ea*) and (ΔH*) values. These results indicate that this tested compound acted as inhibitors through increasing activation energy of copper dissolution by making a barrier to mass and charge transfer by their adsorption on copper surface. The increase in the activation enthalpy (ΔH*) in the presence of the inhibitors implies that the addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. Also, the entropy ΔS* widely decreases with the content of the inhibitor. This means the formation of an ordered stable layer of inhibitor on copper surface (25).

Table 3. Data of weight loss measurements for copper in 1 M HNO_3 solution in the absence and presence of different concentrations of cefotaxime at 25–45 ±1°C.

Conc.	Temp., °C	C.R., mg cm^2min^{-1}	θ	% IE
$0.5x10^{-4}M$	25	0.271	0.589	58.9
	35	0.415	0.541	54.1
	45	0.652	0.532	53.2
	55	0.772	0.506	50.6
$2x10^{-4}M$	25	0.235	0.726	72.6
	35	0.392	0.663	66.3
	45	0.599	0.652	65.2
	55	0.842	0.644	64.4
$4x10^{-4}M$	25	0.174	0.777	77.7
	35	0.199	0.757	75.7
	45	0.447	0.735	73.5
	55	0.599	0.642	64.2
$6x10^{-4}M$	25	0.132	0.864	86.4
	35	0.107	0.856	85.6
	45	0.319	0.824	82.4
	55	0.464	0.742	74.2
$8x10^{-4}M$	25	0.072	0.886	88.6
	35	0.059	0.868	86.8
	45	0.012	0.850	85.0
	55	0.010	0.793	79.3

Table 4. Effect of concentration of cefotaxime on the activation energy of copper dissolution in 1 M HNO_3

Conc. M	**Activation parameters**		
	Ea * kJ mol $^{-1}$	**ΔH* kJ mol $^{-1}$**	**ΔS* J mol^{-1} K^{-1}**
1 M HNO_3	44.32	40.36	-139.13
$0.5x10^{-4}M$	78.83	81.42	-9.52
$2x10^{-4}M$	86.21	85.05	-10.55
$4x10^{-4}M$	83.38	89.34	-13.13
$6x10^{-4}M$	84.92	90.98	-16.93
$8x10^{-4}M$	86.28	99.04	-38.46

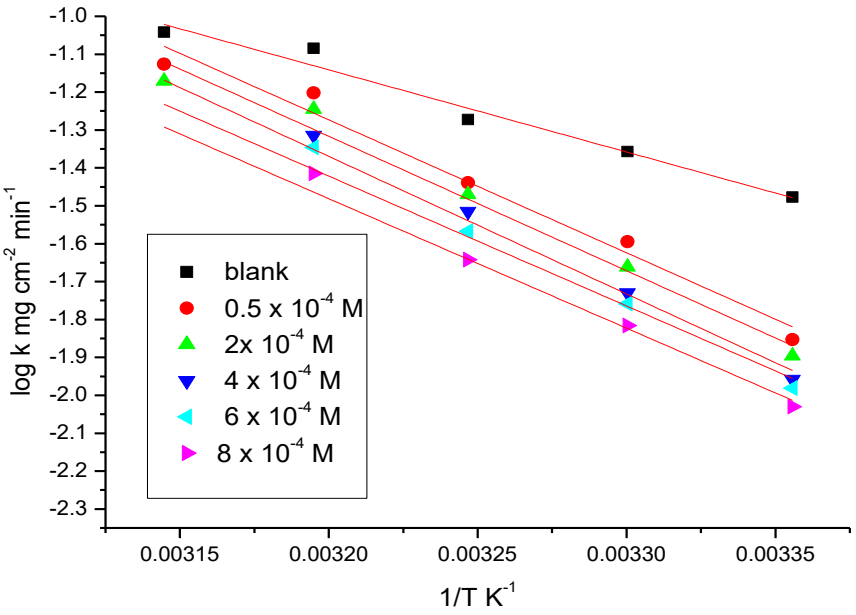


Figure 2. log corrosion rate vs 1/T curves for copper dissolution in 1M HNO_3 in absence and presence of different concentrations of cefotaxime.

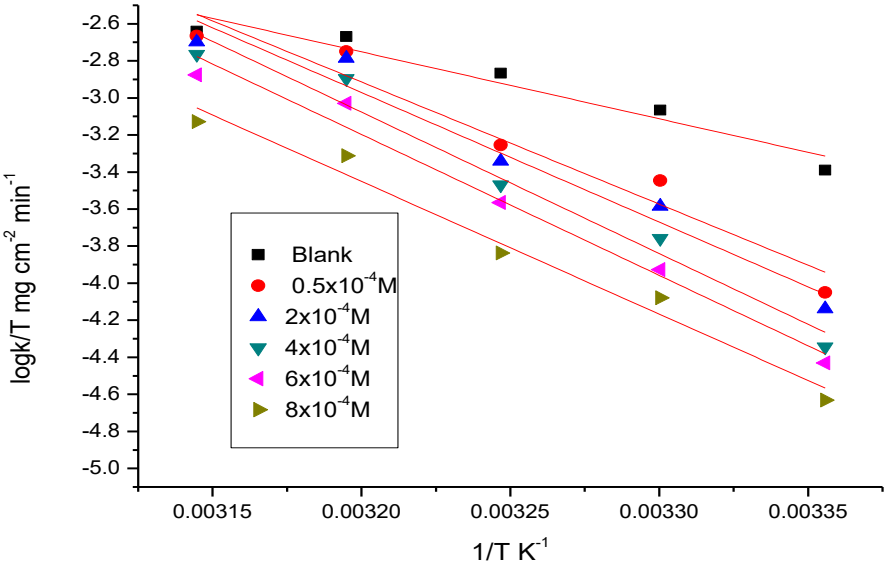


Figure 3. log corrosion rate vs 1/T curves for copper dissolution in 1 M HNO_3 in absence and presence of different concentrations of cefotaxime.

3.1.2.Adsorption isotherm

A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experiment data of the present work.

The degree of surface coverage (θ), i.e, the fraction of the surface covered by the inhibitor molecules at any given concentration of the inhibitor, was calculated from the equation mentioned %IE = (100x θ). The values of θ have been shown in Tables (2, 3). The degree of surface coverage was found to increase with increasing concentration of additives. Attempts were made to fit θ values to various isotherms including Langmuir, Freundlich, Temkin and Frumkin. By far, the best fit was obtained with Langmuir isotherm.

The equilibrium constant of the adsorption process, K, which is related to the standard free energy of adsorption ($\Delta G°_{ads}$) by (26, 27):

$$\frac{\theta}{1-\theta} = KC \qquad (6)$$

$$K = \frac{1}{55.5} e^{\frac{-\Delta G^{\circ}_{ads}}{RT}} \qquad (7)$$

Where 55.5 is the concentration of water molecule in (mol L^{-1}) at metal/solution interface, R is the universal gas constant and T is the absolute temperature.

Figure (4) shows the plot of θ /1- θ vs. C for different concentrations of investigated compound. This plots gives straight line with slope very close to unity. The regression (R^2) is more than 0.9. This means that there is no interaction between the adsorbed species on the electrode surface (28).

All the calculated thermodynamic parameters are listed in Table 5. The negative value of $\Delta G°_{ads}$ in Table 5 suggested that the adsorption of inhibitor molecules on to copper surface is spontaneous process. Generally, values of $\Delta G°_{ads}$ up to -20kJ mol^{-1} are consistent with electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol^{-1} involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (29, 30).

Moreover, the adsorption heat can be calculated according to the Van't Hoff equation 7 (31):

$$\ln K = -\frac{\Delta H^{o}_{ads}}{RT} + const \qquad (8)$$

The ΔH°_{ads} values (Table 5) are negative, which show that the adsorption is an exothermic process (32).

Finally, the standard adsorption entropy $\Delta S°_{ads}$ can be calculated by the equation 9:

$$\Delta S^{o}_{ads} = \frac{\Delta H^{o}_{ads} - \Delta G^{o}_{ads}}{T} \qquad (9)$$

The ΔS°_{ads} values (Table 5) are negative, which show that the adsorption is an exothermic process and always accompanied by a decrease of entropy. The reason can be explained as follows: the adsorption of organic inhibitor molecules from the aqueous solution. Table 5 lists all the above calculated thermodynamic parameters (33-34).

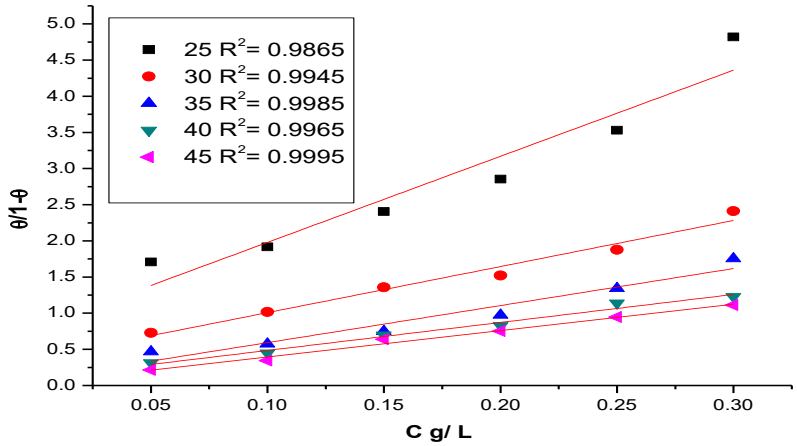


Figure 4. Adsorption isotherm curves for the adsorption of cefotaxime on copper in 1 M HNO_3 at different temperatures.

Table 5. Thermodynamic parameters for copper in 1 M HNO_3 for cefotaxime at 25-45 ± 1°C.

Temp., K	K_{ads}, $g^{-1}l$	ΔG°_{ads}, kJ mol $^{-1}$	ΔH°_{ads}, kJ mol $^{-1}$	ΔS°_{ads}, J mol^{-1} K^{-1}
298	50.62	-19.68	-79.30	-275.83
303	13.45	-16.27		-270.25
308	9.15	-15.66		-266.77
313	7.79	-14.17		-252.71
318	4.17	-13.58		-248.45

3.2.Polarization Curves

Figure (5) shows the potentiodynamic polarization curves for copper dissolution in 1 M HNO_3 in the absence and presence of different concentrations of cefotaxime at 25°C.

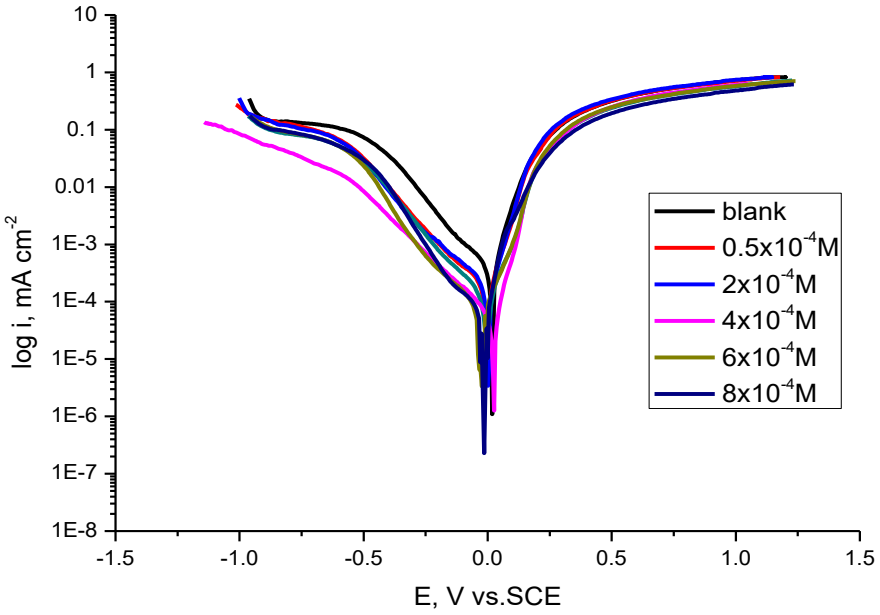


Figure 5. Potentiodynamic polarization curves for the corrosion of copper in 1 M HNO_3 solution without and with various concentrations of cefotaxime at 25±1˚C.

The numerical values of the variation of the corrosion current density (i_{corr}), the corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), the degree of surface coverage (θ), and the inhibition efficiency (%IE) with different concentrations of inhibitor for copper and brass are given in Table (6). The potentiodynamic curves show that there is a clear reduction of both anodic and cathodic currents in the presence of inhibitor compared to those for the blank solution. It is clear that the cathodic reduction (hydrogen evolution) and the anodic reaction (metal dissolution) were inhibited. The values of cathodic Tafel slope (β_c) for inhibitor are found to increase in the presence of inhibitor. The Tafel slope variation suggests that the investigated inhibitor influence the kinetic of the hydrogen evolution reaction (34). This indicates an increase in the energy barrier for proton discharge, leading to less gas evolution (35). The approximately constant values of β_a for inhibitors indicate that these compounds were first adsorbed onto the electrode (copper) surface and impeded by merely blocking the reaction sites of the electrode surface without affecting the anodic reaction mechanism (36). The small changes in corrosion potential, E_{corr}, which indicate that this extract is act as mixed type but mainly cathodic inhibitors for copper corrosion in 1 M HNO_3 solution. The orders of inhibition efficiency of this inhibitor at different concentrations as given by

polarization measurements are in good agreement with those obtained from weight-loss measurements.

Table 6. Effect of concentration of cefotaxime on the electrochemical parameters calculated by potentiodynamic polarization technique for the corrosion of copper in 1 M HNO_3 at 25±1˚C.

Conc., M	i_{corr}, μAcm^2	$-E_{corr}$, mV vs. SCE	β_a, $Vdec^1$	β_c, $Vdec^1$	CR, mpy	θ	%IE
1 M HNO_3	478.0	-20.68	132.5	233	186.2	---	---
0.5X 10^{-4}	192.0	2.22	91.2	234	82.8	0.503	50.3
2X 10^{-4}	153.0	-2.84	90.9	234	76.5	0.590	59.0
4X 10^{-4}	127	4.09	107.8	220	54.6	0.688	68.8
6X 10^{-4}	65.4	25.80	85.4	282	34.5	0.796	79.6
8X 10^{-4}	41.7	26.20	99.4	180.7	13.7	0.875	87.5

3.3.Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of copper in nitric acid solution, in the absence and presence of different concentrations of cefotaxime, is also investigated by EIS at 25 °C after 30 min of immersion Figures(6,7).

EIS spectra of the these compounds were analyzed using the equivalent circuit in Figure 8, where R_s represents the solution resistance, R_{ct} denotes the charge-transfer resistance, and a CPE instead of a pure capacitor represents the interfacial capacitance (37). The impedance of a CPE is described by the following equation:

$$Z_{CPE} = Y_0^{-1}(j\omega_{max})^{-n} \quad (10)$$

Where Y_0 is the magnitude of the CPE, j is an imaginary number, ω is the angular frequency ($\omega_{max} = 2\pi f_{max}$), f_{max} is the frequency at which the imaginary component of the impedance reaches its maximum values, and n is the deviation parameter of the CPE: $-1 \leq n \leq 1$. The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Y_0 and n using equation(38):

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (11)$$

After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charged-transfer controlled (39, 40). The general shape of the curves is very similar for all samples (in presence or in absence of inhibitors at different immersion times) indicating that no change in the corrosion mechanism (41).

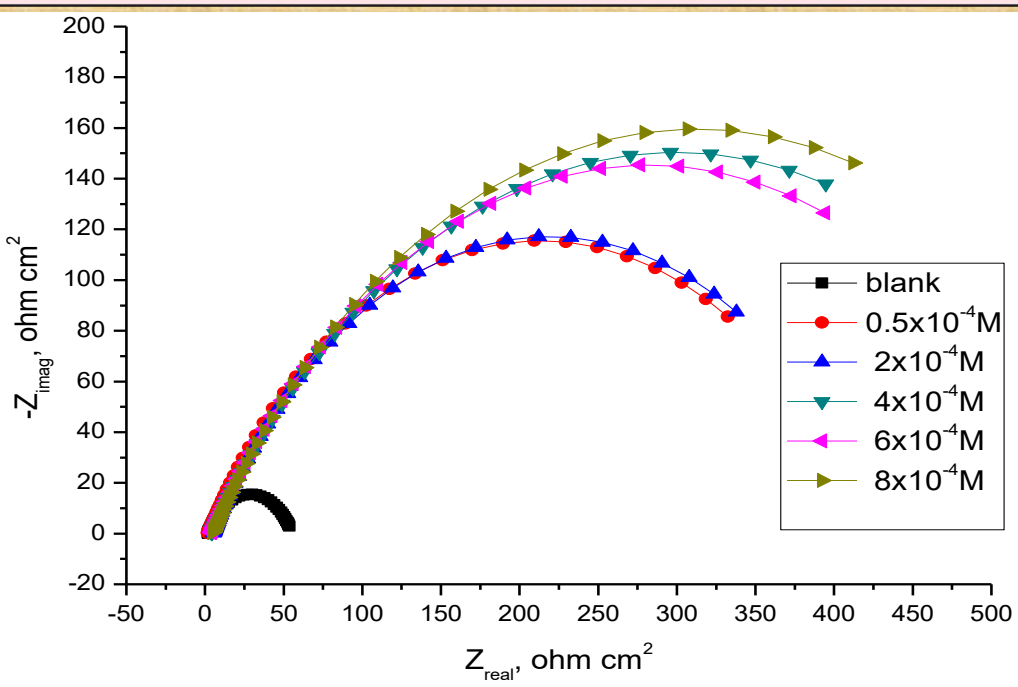


Figure 6. Nyquist plots recorded for copper in 1 M HNO_3 without and with various concentrations of cefotaxime at 25±1˚C.

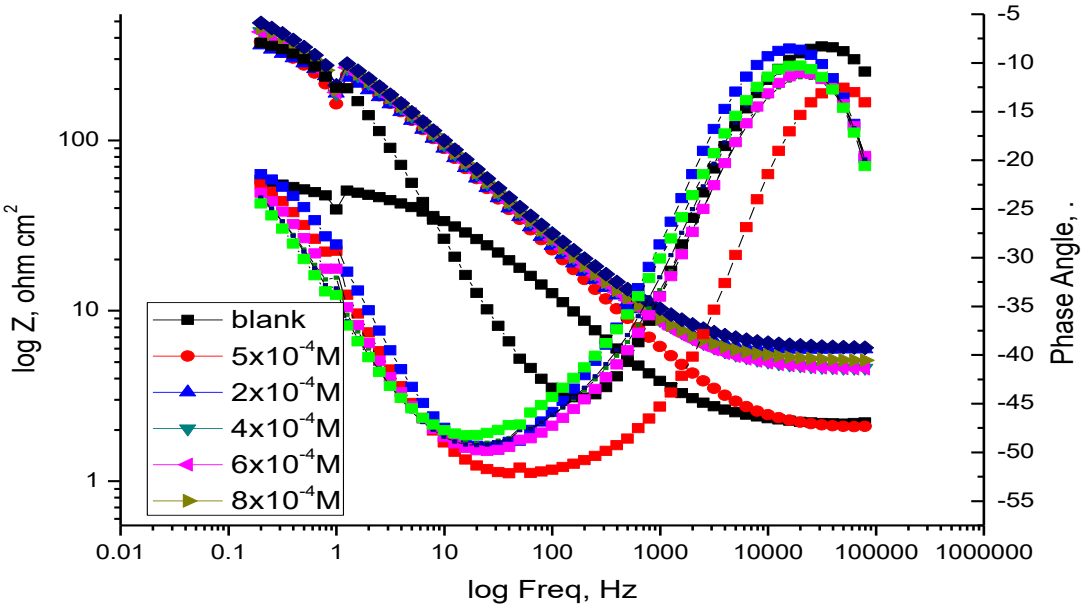


Figure 7. Bode plots recorded for copper in 1 M HNO_3 without and with various concentrations of cefotaxime at 25±1˚C.

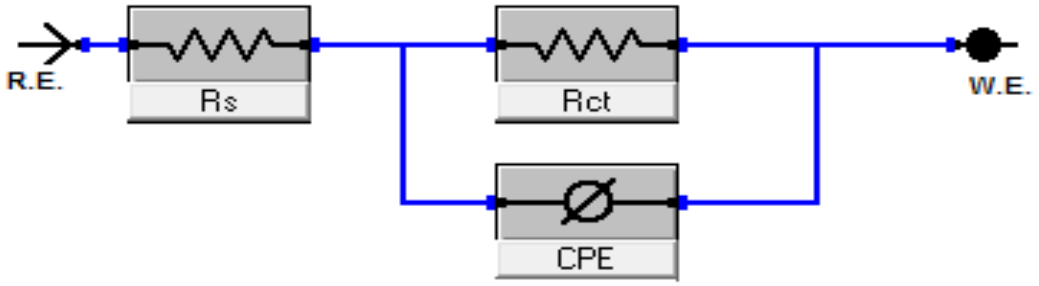


Figure 8. Electrical equivalent circuit used to fit the impedance data

The charge-transfer resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal (-Zmax) are determined. The impedance parameters derived from these investigations are summarized in Table (7). The results obtained from Table (7) reveals that the presence of the cefotaxime led to decreasing the values of C_{dl} due to the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer. It was suggested that the inhibitor molecules were functioned by adsorption at the metal / solution interface. Thus, the decrease in C_{dl} values and the increase in R_{ct} values and consequently, the inhibition efficiency may be reported as the gradual replacement of water molecules by the adsorption of the inhibitor molecules from the metal surface, and by decreasing the extent of dissolution reaction.

Table 7. Electrochemical kinetic parameters obtained from EIS technique for copper in 1 M HNO_3 solution containing various concentrations of cefotaxime at 25±1˚C.

Conc.,M,	R_{ct}, Ω cm^2	C_{dl}, μF cm^{-2}	θ	%IE
1 M HNO_3	53.51	270	--	--
$0.5X10^{-4}$M	426.70	189	0.875	87.5
$2X10^{-4}$M	423.64	190	0.874	87.4
$4X10^{-4}$M	556.60	149	0.904	90.4
$6X10^{-4}$M	591.04	145	0.909	90.9
$8X10^{-4}$M	615.06	136	0.913	91.3

3.4.Mechanism of inhibition

Ulick R. Even, the British scientist who is considered the "father of corrosion sience", has said that "corrosion is largely an electrochemical phenomenon, corrosion in an aqueous environment and in an atmospheric environment (which also involves thin aqueous layer) is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution.

So its progress may be studied by measuring the changes which occur in metal potential with time or with applied electrical currents. Basically, an anode (site for an oxidation that produces electrons in the metal), a cathode (site for reduction that consumes electrons produced by the anodic reaction), an electrolyte (electric conductive environment), and a circuit connecting the anode and the cathode are required for corrosion to occur, the corroding piece of metal is described as a " mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface (i.e., the mixed electrode is a complete electrochemical cell on one metal surface). The general reaction that occurs electrochemically at the anode is the dissolution of metal as ions to form either soluble ionic products or an insoluble compound of the metal, usually an oxide.

$$M \longrightarrow M^{n+} + e^{n-}$$

Where M=metal involved, n= valance of the corroding metal species and

Anodic dissolution of copper usually undergoes two electrochemical transformations:

$$Cu_{(s)} \longrightarrow Cu^{+} + e^{-} \qquad E^{o} = -0.52\ V$$

$$Cu^{+} \longrightarrow Cu^{2+} + e^{-} \qquad E^{o} = 0.16\ V$$

The copper will then dissolve until either all the oxygen is removed or an oxide film stops the process. That is the reaction why the cathodic reaction is predominant for the copper.

Even though the copper undergoes teo reactions (oxidation of copper), this can be summarized as:

$$Cu \longrightarrow Cu^{2+} + 2e^{-} \qquad E^{o} = 0.37\ V$$

The loss of electrons or oxidation at the anode flow through the metallic circuit to the cathode and permit a cathodic reaction to occur, where at a cathodic site, the electrons react with some reducible component of the electrolyte and are themselves removed from the metal.

In alkaline and netral aerated solution (i.e. presence of oxygen in the water) the predominant catodic reaction is the reduction of dissolved oxygen gas [6] which will occur due to its higher potential:

$$O_{2(g)} + 4H^+ + 4e^- \longrightarrow 2\,H_2O(g) \qquad E^o = 1.23\ V$$

Or $O_{2(g)} + 4H_3O^+ + 4\,e^- \longrightarrow 6H_2O$

For metals corroding in acidic solutions (‹ PH4), the supporting cathodic half- reaction tends to be hydrogen ion reduction:

$2H^+ + 2e^- \longrightarrow H_{2\,(g)}$

In aerated acids, the cathodic reactions could be

$O_2 + 4H^- + 4e^- \longrightarrow 2H_2O$

The rates of the anodic and cathodic reactions (the rates of electron production and consumption)., of course, must be equivalent according to faraday's law, being determined by the total flow of electrons from corroding anodes to non-corroding cathodes which is called the "corrosion current", I_{corr} (i.e., a buildup of charge would occur). The driving force for electrons to flow from the anode to the cathode is the difference in potential between the anodic and cathodic site.

Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate(42).

Most organic inhibitors contain at least one polar group with an atom of nitrogen or sulphur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center (43).

With increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened (44, 45). Cefotaxime is organic compound that have center for π-electron and presence of hetero atoms such as oxygen and nitrogen; hence, the adsorption of the inhibitor on the surface on copper is enhanced by their presence. The inhibition efficiency cefotaxime is due to the formation of multi-molecular layer of adsorption between copper cefotaxime. Results of the present study have shown that cefotaxime inhibits the acid induced corrosion of copper by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, inhibitor concentration, and temperature as well as inhibitor adsorption abilities, which is so much dependent on the number of adsorption sites. The mode of adsorption (physiosorption) observed could be attributed to the fact that cefotaxime can be

adsorbed physically. This observation may derive the fact that adsorbed organic molecules can influence the behaviour of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes (44).

4.CONCLUSIONS

From the overall experimental results the following conclusions can be deduced. The main conclusions are as follows:

1. cefotaxime shows good inhibitive action against the corrosion of copper in 1 M HNO_3.The value of inhibition efficiency increases with increasing the inhibitor concentration and decreases with increasing of the temperature.
2. The adsorption of cefotaxime on copper is physical adsorption and obeys Langmuir adsorption isotherm.
3. The negative values of the free energy of adsorption and adsorption heat are indicate that the process was spontaneous and exothermic.
4. cefotaxime is good inhibitor and act mixed type but mainly cathodic inhibitors for copper corrosion in 1 M HNO_3 solution.
5. There is good agreement between the data obtained from chemical method and electrochemical methods.

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