PHARMACEUTICAL COMPOUNDS AS SAVE CORROSION INHIBITORS FOR CARBON STEEL IN 1 M H₂SO₄ SOLUTION

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ABSTRACT

Inhibition performance of Lornoxicam & Tenoxicam against corrosion of C- steel in 1 M H₂SO₄ solution was investigated by weight loss and electrochemical measurements. The inhibition efficiency increased with increasing inhibitor's concentration, but decreased with increase in temperature. Potentiodynamic polarization curves showed that, the inhibitors were of mixed type. The apparent activation energy (E_a^*) and other thermodynamic parameters for the corrosion process have also been calculated. The inhibition of carbon steel corrosion is due to the adsorption of the inhibitor molecules on the surface, which follows Temkin adsorption isotherm. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

INTRODUCTION

Acid solutions are widely used in various industrial processes such as oil well acidification, the petrochemical processes, acid pickling and acidic cleaning [Keles, et al., (2008); Wang, et al., (2003) and El-Maksoud, el al., (2005)], which generally leads to serious metallic corrosion. As the most

effective and economic method, inhibitors are applied in these acid solutions to control the metal dissolution [**Lagrenee et al., (2002) and Abdallah et al., (2003)**]. There is a considerable amount of effort devoted to develop novel and efficient corrosion inhibitors. Organic compounds usually serve as inhibitors, and generally protect the metal from corrosion by forming a protection film on the metal surface [**Obot, et al., (2010)**].

The most effective and efficient inhibitors are the organic compounds that have π bonds, heteroatoms (P, S, N, and O), and inorganic compounds, such as CrO_4^{--}, $Cr_2O_7^{--}$, NO_2^{-}, and so on [**Lece, et al., (2008); Mu, et al., (2006); Samiento-Bustos, et al., (2008); Bastos, et al., (2006); Sahin et al., (2008) and Gece, (2008)**]. However, the use of these compounds has been questioned lately, due to the several negative effects they have caused in the environment [**Broussard, et al., (1997)**]. Thus, the development of the novel corrosion inhibitors of natural source and non-toxic type has been considered to be more important and desirable [**Raja, et al., (2008)**]. Because of their natural origin [**Newman, et al., (2003); Newman, et al., (2007) and Harvey et al., (2008)**], as well as their non-toxic characteristics [**Struck, et al., (2008)**] and negligible negative impacts on the aquatic environment [**Enick, et al., (2006)**], drugs (chemical medicines) seem to be ideal candidates to replace traditional toxic corrosion inhibitors.

The use of environmental friendly pharmaceutical compounds (Lornoxicam and Tenoxicam) as corrosion inhibitors for C-steel has not been reported before. So, our aim is to study the inhibiting effect of these pharmaceutical compounds on C-steel corrosion in H_2SO_4 solution using various chemical and electrochemical techniques.
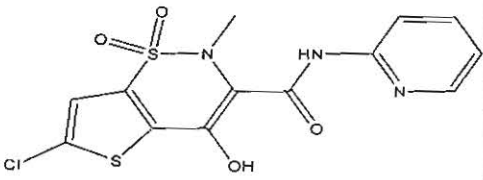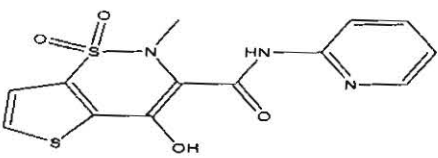
EXPERIMENTAL

1. Materials

Carbon steel containing 0.200 wt % C, 0.350 wt % Mn, 0.024 wt % P, 0.003 wt % Si and balance Fe was used for weight-loss and electrochemical tests, for weight loss tests, the rectangular coupons with

size of 2 x 2 x 0.2 cm were used. A columned steel specimen, embedded in Teflon holder using epoxy resin with an exposed area of 1 cm², was used as the working electrode for electrochemical measurements. The coupons and electrodes were abraded with SiC paper (up to 1200 grit), cleaned with ethanol [Kamis et al., (1991)] and washed with bidistilled water and finally dried at room temperature before being immersed in the acid solutions. The acid solutions used in the work were prepared from analytical grade H_2SO_4. The concentration of the inhibitors was ranged from 10-50 ppm. Lornoxicam & Tenoxicam used in this work have the structures and molecular weights listed in Table (1).

Table (1): Structure and molecular weights of the studied Lornoxicam & Tenoxicam

No.	Name	Structure	Mol.wt.& Mol. Formula
1	6-Chloro-4-hydroxy-2-methyl-N-2-pyridinyl-2H-thieno[2,3-e]-1,2-thiazine-3-carboxamide 1,1-dioxide	Lornoxicam	$C_{13}H_{10}ClN_3O_4S_2$ 371.82
2	4-hydroxy-2-methyl-N-2-pyridinyl-2H-thieno[2,3-e]-1,2-thiazine-3-carboxamide 1,1-dioxide	Tenoxicam	$C_{13}H_{11}N_3O_4S_2$ 337.37

2. Methods
2.1. Chemical technique (weight loss method)

Weight loss measurements were carried out in glass beakers containing 100 ml solution without and with different concentrations of inhibitors in 0.5 M H_2SO_4 solutions. After 3 hours of immersion in the acid solutions in air without bubbling, the samples were taken out and carefully washed with bidistilled water and ethanol, and then dried and weighed. The average weight loss at a certain time for each set of the six samples was taken. The weight loss was recorded to nearest 0.0001 g.

2.2. Electrochemical techniques
2.2.1. Potentiodynamic polarization technique

Potentiodynamic measurements were conducted in a conventional three-electrode glass cell of capacity 100 ml. Three different types of electrodes were used; saturated calomel electrode (SCE) and a platinum foil were used as reference and auxiliary electrodes, respectively. The working electrode was C- steel electrode, which cut from C- steel sheets with thickness 0.2cm. The electrode was of dimensions 1cm x 1cm and was weld from one side to a copper wire used for electric connection. The sample was embedded in a glass tube using epoxy resin [**Fouda et al., (1990)**]. The electrode was prepared before immersion in the test solution as in case of weight loss method. A constant quantity of the test solution (100 ml) was taken in the polarization cell. A time interval of about 30 minutes was given for the system to attain a steady state. All the experiments were carried out at $30\pm1°C$ by using an ultra circulating thermostat. The potentiodynamic current potential curves were recorded by changing the electrode potential automatically from - 500 to + 800 mV versus open circuit potential (E_{ocp}) with a scan rate of 0.5 mV s^{-1} using an electrochemical measurement system Potentiostat / Galvanostat / ZRA (Gamry PCI 300/4). This includes Gamry Framework system based on the ESA400, and a personal computer with DC 105 software for dc corrosion measurements. Echem Analyst software 5.1 was used for plotting, graphing and fitting data.

2.2.2. Electrochemical impedance spectroscopy technique (EIS)

The cell and the apparatus used in electrochemical impedance spectroscopy (EIS) technique is the same as used in potentiodynamic polarization technique with the same reference, auxiliary and working electrodes. After the determination of steady-state current at a given potential, since wave voltage (5 mV) peak to peak, at frequencies between 100 KHz and 10 mHz were superimposed on the rest potential. Gamry applications that include EIS300 for electrochemical impedance spectroscopy along with a computer for collecting data. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. All the potentials reported are referred to SCE. The impedance diagrams are given in the Nyquist and Bode representations.

RESULTS AND DISCUSSION

1. Weight loss measurements

The weight loss (mg cm^{-2}) of C-steel was determined at various time intervals, in the absence and presence of different concentrations of the specified pharmaceutical compounds. Figure (1) shows the weight loss-time curves for C-steel corrosion at 30 °C at various concentrations of Lornoxicam (the more effective than Tenoxicam). Similar curves were obtained for Tenoxicam (not shown). It is obvious that the weight loss of C- steel in the presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process **[Fouda et al., (1990)]**. The inhibition efficiency (% η) and the surface coverage (θ) that represents the weight of the metal surface covered by inhibitor molecules were calculated using the following equation:

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

where ΔW_{free} and ΔW_{inh} are the weight losses per unit area in the absence and presence of inhibitors, respectively. The calculated values of % η and θ are summarized in Table (2). Careful inspection of these results showed that, the increase in the inhibitor concentration was accompanied by a decrease in weight-loss and an increase in the percentage inhibition (% η). These results led to the conclusion that, these compounds under investigation are fairly efficient as inhibitors for C-steel dissolution in sulphuric acid solution. Also the degree of surface coverage (θ) by the inhibitor would increase by increasing the inhibitor concentration. This behavior could be attributed to increase of the number of adsorbed molecules at metal surface [**Otieno-Alego, et al., (1992)**]. With high inhibitor concentration, a compact and coherent inhibitor over film is formed on the C- steel which reduces chemical attacks on the metal. From data, the inhibition efficiency (% η) has the following order: Lornoxicam > Tenoxicam.
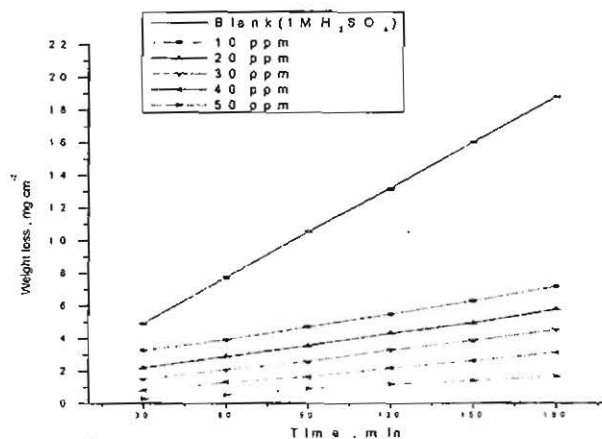

Fig. (1): Weight loss-time curves for the corrosion of C- steel in 1 M H_2SO_4 in the absence and presence of different concentrations of Lornoxicam at 30°C

Table (2): Surface coverage and inhibition efficiency at different concentrations of Lornoxicam and Tenoxicam for the corrosion of C-steel after 120 min immersion in 1 M H_2SO_4 at 30°C

Conc.	Lornoxicam		Tenoxicam	
Ppm	θ	% η	θ	% η
10	0.585	58.5	0.298	29.8
20	0.672	67.2	0.389	38.9
30	0.751	75.1	0.473	47.3
40	0.834	83.4	0.599	59.9
50	0.911	91.1	0.697	69.7

2. Adsorption isotherm

Corrosion inhibitors are found to protect steel corrosion in acid solutions by adsorbing themselves on steel surface. Moreover, the adsorption process depends on the chemical composition of the molecules, the temperature and the electrochemical potentials at the metal/solution interface. Adsorption is a separation process involving two types: i) physisorption which involves electrostatic forces between ionic charges at the metal/solution interface. The heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperatures and ii) Chemisorption which involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a co-ordinate type bond [**Sahin, et al., (2002)**]. Chemisorption is typified by much stronger adsorption energy than physical adsorption. Such a bond is therefore more stable at higher temperatures. Various adsorption isotherms including Frumkin, Langmuir, Temkin and Freundlich isotherms were tested to find the best suitable adsorption isotherm for

adsorption of the studied inhibitors on the C- steel surface. Temkin adsorption isotherm was found to fit the experimental data. Temkin mathematical expression is given as follows [Bosch, et al., (2001)]:

$$\Theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C_{inh.}$$

(2)

where $C_{inh.}$ is the inhibitor bulk concentration in (ppm), K_{ads} (M^{-1}) is the equilibrium constant of adsorption and (f) is the Temkin heterogeneity factor which is related to Frumkin lateral interaction factor a (f = -2a). (a) is the factor that describe the molecular interactions in the adsorbed layer. From the intercepts of the straight lines on the Θ-axis (Fig. 2 for Lornoxicam for example), K_{ads} can be calculated.

Also, some thermodynamic adsorption parameters were calculated. The well known thermodynamic adsorption parameters are the standard free energy of adsorption (ΔG°_{ads}), the heat of adsorption (ΔH°_{ads}) and the entropy of adsorption (ΔS°_{ads}). These quantities can be calculated by various mathematical methods depending on the estimated values of K_{ads} from adsorption isotherms at different temperatures. It is well known that K_{ads} represents the strength between adsorbate and adsorbent. Large values of K_{ads} mean better inhibition efficiency of the inhibitors, i.e., strong electrical interaction between the double-layer existing at the phase boundary and the adsorbing inhibitor molecules (which is in our case). Small values of K_{ads}, however, reveal that such interactions between adsorbing inhibitor molecules and the metal surface are weaker, indicating that the inhibitor molecules are easily removable by the solvent molecules from the metal surface [Finely, et al., (1960)].

The ΔG°_{ads} values at all studied temperatures can be calculated from Eq. (3) where one molecule of water is replaced by one molecule of inhibitor [Amin, et al., (2009)]:

$$K_{ads} = (1/55.5) \exp(-\Delta G^{\circ}_{ads}/RT) \tag{3}$$

where 55.5 is the concentration of water in mol l^{-1}. The heat of adsorption (ΔH°_{ads}) could be calculated according to the Van't Hoff equation [MBockris, et al., (1964)]:

$$\log K_{ads} = (- \Delta H^\circ_{ads} / 2.303RT) + \text{constant} \tag{4}$$

In order to calculate the heat of adsorption (ΔH°_{ads}), ($\log K_{ads}$) was plotted against (1/T) as shown in Figure (3). The straight lines were obtained with slope equal to ($-\Delta H^\circ_{ads}/R$). Then in accordance with the basic equation:

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \tag{5}$$

By introducing the obtained ΔG°_{ads} and ΔH°_{ads} values in Eq. (5), the entropy of adsorption (ΔS°_{ads}) values were calculated at all studied temperatures. All estimated thermodynamic adsorption parameters for studied pharmaceutical compounds on C- steel from 1 M H_2SO_4 solution were listed in Table (3). From the data it can be concluded that:

i) The experimental data give good curves fitting for the applied adsorption isotherms as the correlation coefficients (R^2) were in the range 0.980-0.997 ii) K_{ads} value decreases with temperature from 30 °C to 60 °C iii) The values of (a) was positive in all cases showing that attraction forces between the adsorbed species on C-steel surface are expected [Lebrini ,et al., (2005)] iv) The negative values of ΔG°_{ads} reflect that the adsorption of Lornoxicam and Tenoxicam on C-steel surface from 1 M H_2SO_4 solution is spontaneous process. v) ΔG°_{ads} may increases (becomes less negative) with an increase of temperature which indicates the occurrence of exothermic process at which adsorption was unfavorable with increasing reaction temperature as the result of the inhibitor desorption from the steel surface [Li, et al., (2006)] vi) It is usually accepted that the value of ΔG°_{ads} around -20 kJ mol^{-1} or lower indicates the electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution (i.e. physisorption) while those around -40 kJ mol^{-1} or higher involve charge sharing or charge transfer from inhibitor molecules to the metal surface to form a co-ordinate type of bond (i.e. chemisorptions) [Mousa, et al., (2009)]. From the obtained values of ΔG°_{ads} it was found that the existence of

comprehensive adsorption (physical and chemical adsorption), that is to say, since the adsorption heat approached the general chemical reaction heat, the chemical adsorption occur:

vii) The negative sign of ΔH°_{ads} reveals that the adsorption of inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption [**Donahuce, et al., (1965)**]. The unshared electron pairs in investigated molecules may interact with d-orbitals of C-steel to provide a protective chemisorbed film [**Smialowska, et al., (1973)**]. In the case of investigated compounds, the absolute values of enthalpy are relatively high, approaching those typical of chemisorption. The values of ΔS°_{ads} in the presence of investigated compounds are large and negative that is accompanied with exothermic adsorption process [**Khamis, et al., (2000)**].
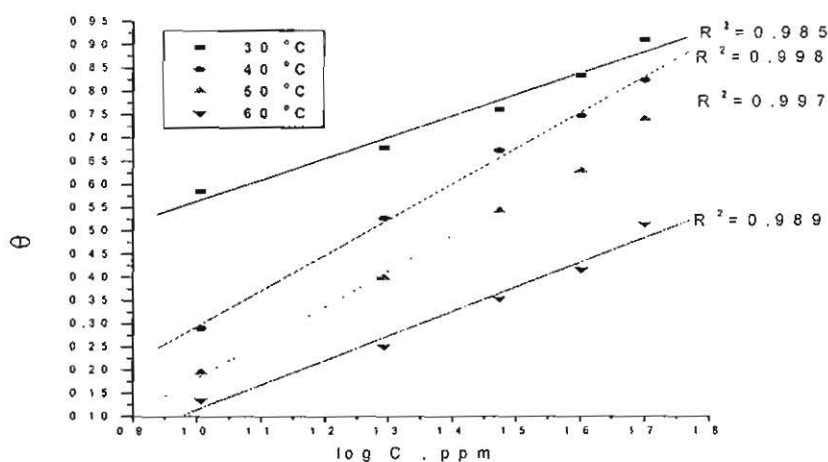

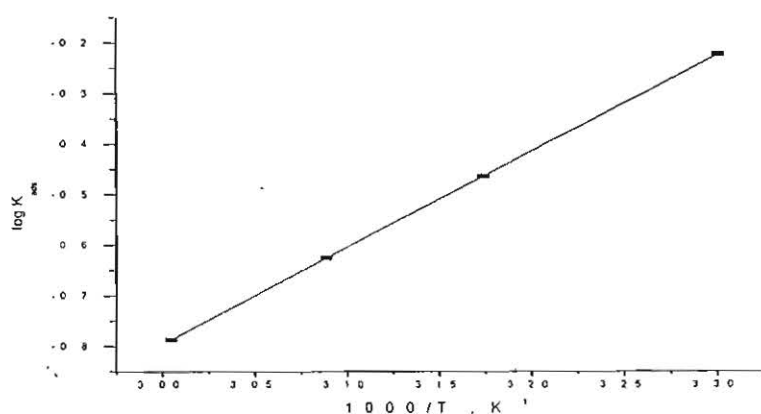**Fig. (2):** Temkin adsorption isotherm of Lornoxicam on C-steel surface in 1 M H_2SO_4 at different temperatures .

Fig. (3) : ($\log k_{ads}$) vs. ($1/T$) for the corrosion of C-steel in 1 M H_2SO_4 in the presence of Lornoxicam at different temperatures

Table (3): Thermodynamic parameters for the adsorption of Lornoxicam and Tenoxicam on C-steel surface in 1 M H_2SO_4 at different temperatures

Temp. °C	$K_{ads}x10^{-3}$ M^{-1}	$-\Delta G°_{ads}x10^{-2}$ $kJ\ mol^{-1}$	$-\Delta H°_{ads}$ $kJ\ mol^{-1}$	$-\Delta S°_{ads}$ $J\ mol^{-1}\ K^{-1}$
Lornoxicam				
30	594.3	88.06	36.3	28.9
40	240.6	67.48	36.3	21.4
50	171.4	60.45	36.3	18.6
60	149.6	58.59	36.3	18.2
Tenoxicam				
30	254.7	66.71	33.4	21.9
40	124.4	50.28	33.4	15.9
50	114.2	49.50	33.4	15.2
60	78.3	40.67	33.4	12.1

3. Effect of temperature

Temperature has a great effect on the rate of metal electro-chemical corrosion as it is the accelerating factor in most of chemical reactions. It increases the energy of the reacted species, as a result, chemical reaction get much faster. The corrosion reaction is a chemical reaction in which the Fe atoms at the metal surface react with the negatively charged anions (OH⁻, SO_4^{2-}, Cl⁻, etc.). Hence, increasing temperature of the environment increases the activation energy of the Fe atoms at the metal surface and accelerates the corrosion process of C-steel in the acidic media. In case of acidic corrosion (hydrogen depolarization), the corrosion rate increases exponentially with temperature increase because the hydrogen evolution overpotential decreases [**Mu, et al., (2005)**].

The effect of temperature on both corrosion and corrosion inhibition of C-steel in 1 M H_2SO_4 solution in absence and presence of Lornoxicam and Tenoxicam at concentrations of 10 - 50 ppm at different temperatures ranging from 30 - 60°C was investigated. The relation between the corrosion rate (k_{corr}) of C-steel in acidic media and temperature (T) is often expressed by the Arrhenius Eq (6) [**Bentiss, et al., (2001); Oguzie, et al., (2005) and Singh, et al., (2010)**].

$$k = A \exp(-E_a^* / RT) \tag{6}$$

where (E_a^*) is the apparent activation energy and (A) is the Arrhenius pre-exponential factor.

A plot of [$\log k_{corr}$] vs. [$1/T$] (Fig. 4) gave straight lines with slope of ($-E_a^*/2.303R$) at which the activation energies were calculated and represented in Table (4).

Activation parameters for corrosion of C-steel in 1 M H_2SO_4 were calculated from transition state- type equation [**Solomon, et al., (2010)**]:

$$k = RT / Nh \exp(\Delta S^*/R) \exp(-\Delta H^* / RT) \tag{7}$$

where (k) is the corrosion rate, (h) is the Planck constant $(6.62 \times 10^{-34}$ Js), (N) is the Avogadro number $(6.022 \times 10^{23} \text{ mol}^{-1})$, (R) is the universal gas constant and (T) is the absolute temperature.

The relation between [log k / T] vs. [1 / T] gives straight lines (Fig. 5) with slope of $(\Delta H^* / 2.303R)$ and an intercept of [log (R/Nh) + $(\Delta S^* / 2.303R)]$ from which the values of the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) can be calculated and listed also in Table (4).

All estimated thermodynamic - kinetic parameters were tabulated in Table (4). The obtained data can be interpreted as follows:
i) in 1 M H_2SO_4 solutions, the addition of lornoxicam and tenoxicam leads to an increase in the apparent activation energy which indicated physical (electrostatic) adsorption **[Khedr, et al., (1992)]**. Furthermore, the activation energy rose with increasing inhibitor concentration, suggesting strong adsorption of inhibitor molecules at the metal surface **[Xu ,et al., (2008)]**. The increase in the activation energy was due to the corrosion reaction mechanism in which charge transfer was blocked by the adsorption of inhibitor molecules on the C-steel surface **[RameshSaliyan, et al., (2008) and Moretti, et al., (2004)]**. It also revealed that the whole process was controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of inhibitors was greater than -20 kJ mol^{-1}**[Li, et al., (2009)]**
ii) The positive sign of the enthalpy of activation (ΔH^*) reflects the endothermic nature of C-steel dissolution process meaning that dissolution of C-steel is difficult **[Bosch, et al., (2001)]**. Also all values of E^*_a are larger than the analogous values of ΔH^* indicating that the corrosion process must involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume **[Shorky, et al., (1998)]** iii) The entropy of activation (ΔS^*) in the absence and presence of inhibitor has large and negative values, this indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that, a

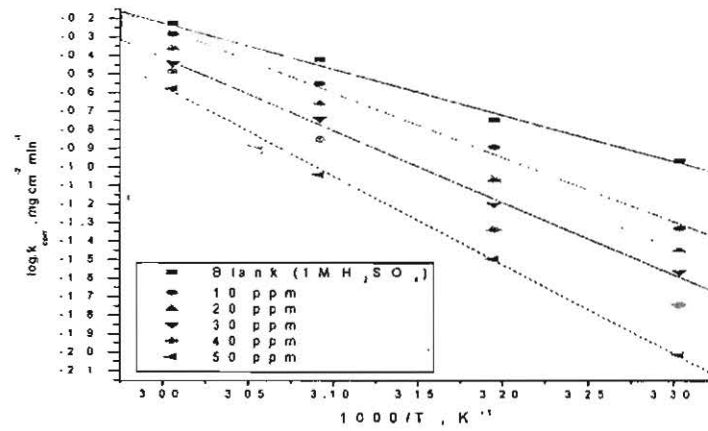decrease in disordering takes place on going from reactants to the activated complex [**Fouda, et al., (2010)**].

Fig. (4): Arrhenius plot for C-steel corrosion rates (k_{corr}) after 120 min immersion in 1 M H_2SO_4 in the absence and presence of various concentrations of Lornoxicam
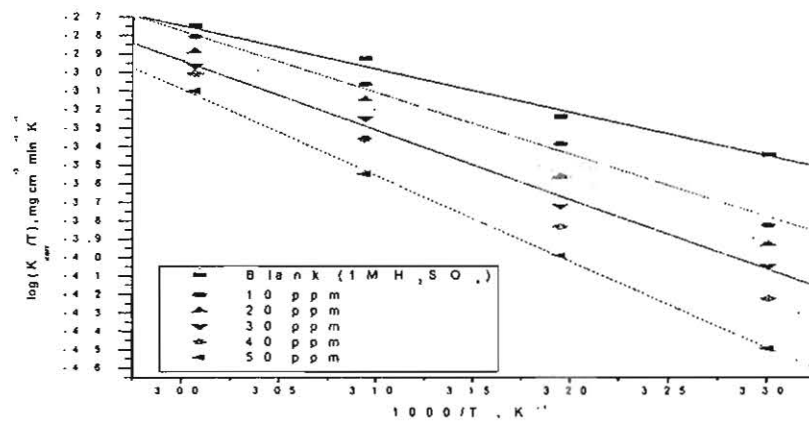

Fig. (5): Transition state plot for C-steel corrosion rates (k_{corr}) in the absence and presence of various concentrations of Lornoxicam.

Table (4): Kinetic-thermodynamic parameters for C- steel corrosion in
the absence and presence of various concentrations of
Lornoxicam and Tenoxicam

Conc. ppm	$A x 10^{-9}$ g cm^{-2} min^{-1}	E^*_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}
Lornoxicam				
Blank	0.2	48.6	46.5	110.2
10	17.7	66.9	65.8	52.7
20	48.7	70.3	69.1	44.9
30	133.2	73.6	72.4	36.3
40	216.3	81.7	80.2	14.1
50	550.8	91.3	89.9	5.9
Tenoxicam				
10	0.1	54.4	52.5	92.8
20	0.3	56.5	54.9	86.2
30	0.6	58.4	56.4	82.7
40	3.1	62.9	60.1	72.5
50	12.2	67.1	64.2	61.8

4. Electrochemical techniques
4.1. Potentiodynamic polarization technique

Polarization measurements were carried out to obtain Tafel plots
in the absence and presence of various concentrations of Lornoxicam and
Tenoxicam. The current-potential relationship for the C-steel electrode at
different test solutions of Lornoxicam is shown in Fig. (6), similar curves
were obtained for Tenoxicam (not shown). The numerical values of the
variation of the corrosion current density (j_{corr}), the corrosion potential
(E_{corr}), the cathodic Tafel slope (β_c) and anodic Tafel slope (β_a), degree of
surface coverage (θ) and the inhibition efficiency (%η) with the
concentrations of inhibitors are listed in Table (5). The results in this
Table indicated that: i) the corrosion current density (j_{corr}) decreases in the
presence of inhibitors compared to the blank solution and also decreased

with increasing concentration of inhibitors. ii) Addition of Lornoxicam and Tenoxicam causes decrease in the corrosion rate, that is, shifts both the anodic and cathodic curves to lower values of current densities. This implies that both the hydrogen evolution and the anodic dissolution reactions of C-steel electrode corrosion are inhibited. This may be due to adsorption of the inhibitor over the corroding surface [**Bockris, et al., (1962)**] iii) the slopes of the anodic and cathodic Tafel lines (β_a & β_c) were slightly changed on increasing the concentration of the tested compounds. This indicates that there is no change of the mechanism of inhibition in presence and absence of inhibitors and that the inhibitor affects both anodic and cathodic reactions [48] i.e. mixed-type. Inhibition efficiency (% η) was calculated using the following equation:

$$\% \eta = [1 - (j_{corr} / j^{\circ}_{corr})] \times 100 \tag{8}$$

where (j_{corr} and j°_{corr}) are the corrosion current densities in the absence and presence of inhibitors, respectively. The order of % η was found to decrease in the following sequence: Lornoxicam > Tenoxicam.
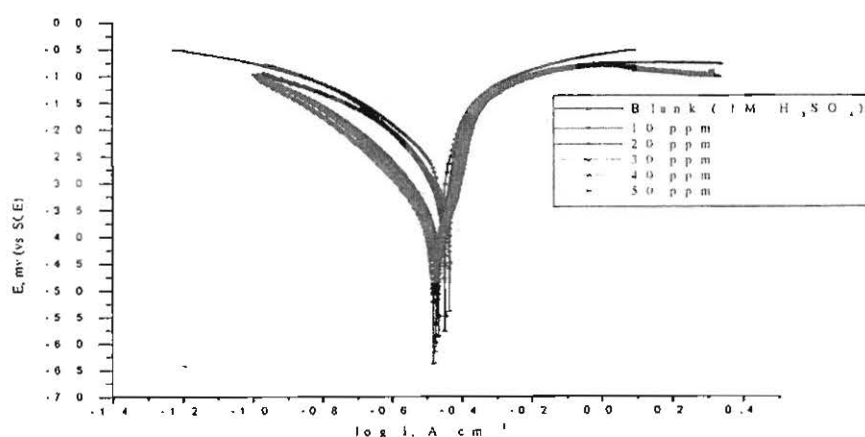

Fig. (6): Potentiodynamic polarization curves for the corrosion of C- steel in 1 M H_2SO_4 in the absence and presence of different concentrations of Lornoxicam at 30°C

Table (5): Potentiodynamic polarization parameters for the corrosion of C- steel in 1 M H_2SO_4 in the absence and presence of different concentrations of Lornoxicam and Tenoxicam at 30°C

Comp.	Conc. ppm	$-E_{corr}$ mV vs. SCE	j_{corr} $\times 10^{-4}$ mA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	R_p $\times 10^{-3}$ Ω cm^2	CR mmy^{-1}	θ	% η
Blank	0.0	458	99.1	479	348	8.8	115.10	------	-----
Lornoxicam	10	436	24.9	271	371	2.7	28.90	0.748	74.8
	20	449	11.0	238	355	5.5	12.86	0.888	88.8
	30	467	5.69	217	308	9.7	6.60	0.942	94.2
	40	474	4.90	208	303	1.1	5.70	0.950	95.0
	50	482	2.61	188	275	1.8	3.10	0.973	97.3
Tenoxicam	10	447	36.8	311	376	2.1	42.70	0.629	62.9
	20	472	31.2	312	437	2.5	36.3	0.685	68.5
	30	456	12.9	265	349	5.0	14.9	0.869	86.9
	40	461	9.27	247	331	6.6	10.7	0.906	90.6
	50	456	6.67	236	306	8.7	7.74	0.933	93.3

4.2. Electrochemical impedance spectroscopy technique (EIS)

EIS measurements were carried out at 30°C in acid solution with and without inhibitors. The equivalent circuit model which describes the metal / electrolyte interface of the present corroding system is shown as insert in Fig. (7), where R_s, R_{ct} and CPE refer to solution resistance, change transfer resistance and constant phase element representing the double layer capacitance (C_{dl}) of the interface, respectively. A typical example of EIS data obtained for Lornoxicam is represented as Nyquist and Bode plots in Fig. (8a and 8b), similar curve was obtained for tenoxicam (not shown). The complex impedance diagram is characterized by a single full semicircular appearance indicating that corrosion of carbon steel is controlled by a charge transfer process [LiX,

et al, (2009)]. Small distortion was observed in the diagrams, this distortion has been attributed to frequency dispersion [**Solmaz ,et al., (2008)**]. The obtained diameters of the capacitive loops increase in presence of inhibitors, and are indicative of the extent of inhibition of corrosion process, contrary to the decrease of the capacity of double layer (C_{dl}) which is defined as:

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

The inhibition efficiencies obtained from the EIS measurements are calculated from the relation:

$$\% \eta_{EIS} = [1 - (R_{ct} / R`_{ct})] \times 100 \tag{10}$$

where R_{ct} and $R`_{ct}$ are the transfer resistance without and with the inhibitor, respectively. The analysis of the EIS parameters shows that R_{ct} increases by increasing the concentration of inhibitors, giving consequently a decrease in the corrosion rate. It is important to emphasize that the values of C_{dl} decrease with increasing the inhibitor concentration. This is due to the gradual replacement of water molecules in the double layer by the adsorbed inhibitor molecules which form an adherent film on the metal surface and leads to decrease in the local dielectric constant of the metal solution interface [**Fouda, et al., (2009)**]. The obtained Bode plot for Lornoxicam is shown in Figure (8b). The high frequency limits corresponds to ($R_{ct} + R_s$). The low frequency contribution shows the kinetic response of charge transfer reaction [**Fouda, et al., (2005)**]. EIS data are shown in Table (6), from this Table, it is clear that the inhibition efficiency (% η_{EIS}) of these compounds follows the same sequence as before: Lornoxicam > Tenoxicam. It can be concluded that the inhibition efficiency from weight loss, polarization curves, electrochemical impedance spectroscopy measurements are in good agreement.
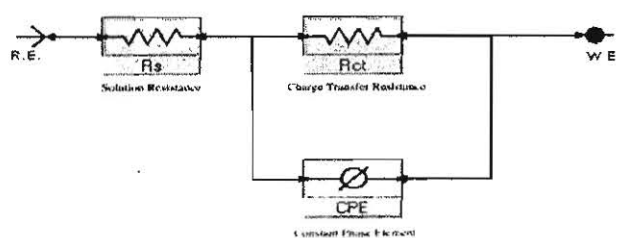
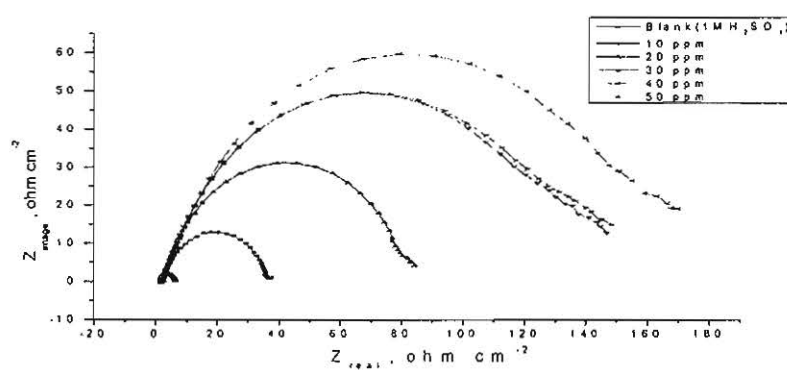Fig. (7): Equivalent circuit model used to fit experimental EIS data recorded for C- steel electrode in 1 M H_2SO_4

Fig. (8a): Nyquist plot for the corrosion of C- steel in 1 M H_2SO_4 in the absence and presence of different concentrations of Lornoxicam at 30°C
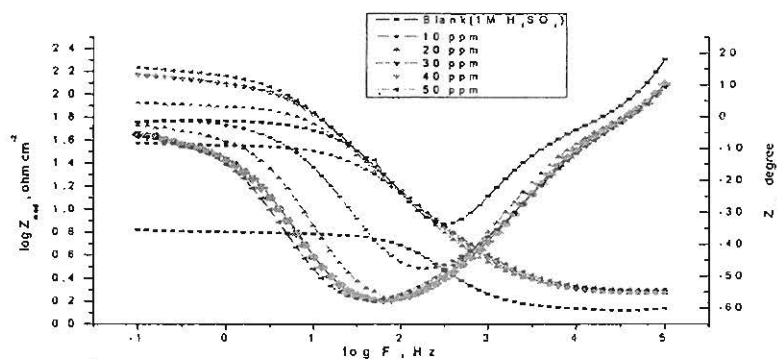
Fig. (8b): Bode plot for the corrosion of C- steel in 1 M H_2SO_4 in the absence and presence of different concentrations of Lornoxicam at 30°C

Table (6): Electrochemical kinetic parameters obtained from EIS technique for the corrosion of C-steel in 1 M H_2SO_4 at different concentrations of Lornoxicam and Tenoxicam at 30° C

Comp.	Conc., ppm	$C_{dl} \times 10^{-2}$, $\mu F\ cm^{-2}$	R_{ct}, $\Omega\ cm^2$	θ	% η
Blank	0.0	20.19	4.99	----	----
Lornoxicam	10	2.86	35.32	0.859	85.9
	20	1.23	82.06	0.939	93.9
	30	0.71	141.8	0.964	96.4
	40	0.70	144.0	0.966	96.6
	50	0.59	171.9	0.971	97.1
Tenoxicam	10	9.50	10.62	0.530	53.0
	20	5.92	17.03	0.706	70.6
	30	5.83	17.30	0.711	71.1
	40	4.42	22.87	0.782	78.2
	50	4.33	23.40	0.787	78.7

5. Mechanism of inhibition

The adsorption of investigated compounds can be attributed to the presence of polar unit having atoms of nitrogen, sulphur and oxygen and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pair of hetero-atoms and π-electrons of aromatic ring [**Ahamad, et al., (2010)**].

From the results obtained using electrochemical and weight loss measurements, it was concluded that the investigated compounds inhibit the corrosion of carbon steel in 1 M H_2SO_4 by adsorption at carbon steel/solution interface. It is general assumption that the adsorption of organic inhibitors at the metal surface interface is the first step in the mechanism of the inhibition action. Organic molecules may be adsorbed on the metal/acid solution interface by one and/or more of the following ways: i) Electrostatic interaction of protonated molecules with already adsorbed chloride ions, ii) Donor-acceptor interactions between the π-electrons of aromatic ring and vacant d-orbital of surface iron atoms and iii) Interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms [**Ishtiaque Ahmad et al, (2010)**].

The inhibition of active dissolution of the metal is due to the adsorption of the inhibitor molecules on the metal surface forming a protective film. The inhibitor molecules can be adsorbed onto the metal surface through electron transfer from the adsorbed species to the vacant electron orbital of low energy in the metal to form a co-ordinate link. The inhibition efficiency depends on many factors [**Bentiss, et al., (2009)**] including the number of adsorption centers, mode of interactions with metal surface, molecular size and structure. It is well known that iron has co-ordination affinity toward nitrogen, sulfur and oxygen-bearing ligands [**Snyder, et al., (1989)**].

The order of inhibition is decreased as the following order: Lornoxicam > Tenoxicam. This is due to its larger molecular size and the presence of Cl group which has a dual effect (acts as electron donor or electron acceptor) and hence Cl atom may act as donor atom which increases the electron charge density on the molecule and hence % η

increases. Tenoxicam is lower in inhibition efficiency than Lornoxicam due to the absence of extra donating atom than in Lornoxicam and also due to the its lower molecular size. ·

CONCLUSION

The results obtained show that Lornoxicam and Tenoxicam are good corrosion inhibitors for C-steel under acidic conditions. Excellent agreement between the inhibition efficiencies calculated using different techniques was obtained. The adsorption of the Lornoxicam and Tenoxicam onto the steel surface was characterized by the decrease in: (i) The cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of Lornoxicam and Tenoxicam, (ii) The weight loss of the coupons immersed in the solutions containing the inhibitors and (iii) The double-layer capacitance computed from electrochemical impedance spectroscopy experiments. The adsorption behavior of the Lornoxicam and Tenoxicam is consistent with Temkin adsorption isotherm. Lornoxicam and Tenoxicam are adsorbed on C-steel surface following physisorption and chemisorption mechanism. The results of polarization indicated that Lornoxicam and Tenoxicam are of mixed type. A good agreement was obtained between all the investigated techniques.

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بعض المركبات الدوائيه كمثبطات لتآكل الصلب الكربونى فى محاليل حمض الكبريتيك

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يعتبر الصلب الكربونى من المعادن المهمه لكونه يستخدم فى كثير من الـصناعات لجودة خصائصه الميكانيكيه ولكنه يواجه مشكلة التآكل وخاصة فى الأوساط الحامضيه وهـذا البحث يناقش كيفية حماية هذا المعدن باستخدام مثبطات صديقة للبيئه وايضا رخيصة الـثمن.

تم استخدام بعض المركبات الدوائيه كمثبطات لتآكل الصلب الكربونى فى ١ مـولر من حمـض الكبريتيـك بطـرق كيميائيـه (فقـد الـوزن) وكهروكيميائيـه (الاسـتقطاب البوتنشوديناميكى والمعاوقه الكهروكيميائيه). أظهرت النتائج ان هذه المركبات تعمل كمثبطات جيده للتآكل. كما وجد ان كفاءة التثبيط تعتمد على تركيز هذه المركبات والتركيب الكيميـائى لها. وقد دلت طريقة الاستقطاب البوتنشوديناميكى على ان هذه المركبات تعمـل كمثبطـات مختلطه (انوديه وكاثوديه) وان ادمصاص هذه المركبات على سطح الصلب الكربونى يتبـع ايزوثيرم تمكن.