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Adsorption and Thermodynamic Studies for Corrosion Inhibition of API 5L X-52 Steel in 2 M HCl Solution by Moxifloxacin

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ABSTRACT

The inhibition of API 5L X-52 steel corrosion in an acidic medium by moxifloxacin at 303 K, 313 K and 323 K was monitored by potentiodynamic polarization measurement. The concentration of acid medium was maintained throughout the experiment. The inhibition efficiency was found to increased with increase in concentration of moxifloxacin and temperature. Activation energy, adsorption and thermodynamic parameters were evaluated from the study temperature. Herein, moxifloxacin brought about a decrease in activation energy E_a that reflects chemisorption. The adsorption of the moxifloxacin on the steel surface was found to obeyed Langmuir adsorption isotherm ΔG_{ads} values, indicating strong and spontaneous adsorption of the moxifloxacin on the surface of API 5L X-52 steel.

***Keywords*:** thermodynamic, corrosion inhibition, API 5L X-52 steel, moxifloxacin and adsorption

1. INTRODUCTION

Corrosion is a process that result from the action of the medium on a particular material, causing its overall, partial, superficial or structural deterioration by an electrochemical, chemical or electrolytic attack. Corrosion tribulations are common in oil and gas industries, where approximately 50 % of materials failures in oil and gas refineries and petrochemical plants are cause by corrosion, which promotes economic, environmental and human life losses [Ferreira *et al.*, 2015]. Corrosion inhibitors are widely used in industries to battle metallic corrosion, they slow down and even eliminate the corrosive processes taking place in the transportation, production and storage of oil and it derivatives. The majority of inhibitors used in industry in acid corrosion are organic compounds consisting of nitrogen, oxygen and sulphur atoms. Inhibitor that contain double or triple bond take an important part in facilitating the adsorption of this compounds onto metal surface. Environmental sustainability concerns and the elevated cost of synthetic inhibitors motivated the search for less expensive and environmentally friendly alternatives such as corrosion inhibitors derive from natural products (Ferreira *et al.*, 2015). In the recent years drugs has been used as corrosion inhibitors [Eddy and Odemela].

Many authors generally agree that drugs are inhibitors that can compete favorably with green corrosion inhibitors, thus Fluoroquinolones was reported by Eddy *et al.*, 2010 as corrosion inhibitor, Ciprofloxacin reported by (Akpan and Offiong, 2014a). The summary of pharmaceutical drugs as corrosion inhibitors include: Amoldipine (Akpan and Offiong, 2014b), Farcolin (Attia, 2015), Voltaren (Abdel Hameed, 2015), Dicloxacillin (Karthikeyan *et al*, 2015), Azithromycin, Abdullatef (2015), Amoxicillin (Siaka *et al.*, 2013). Cefixime., (Naqvi *et al.*, 2011) and Erythromycin (Eddy *et al*., 2010). Research efforts have been done recently on the use of moxifloxacin drugs as corrosion inhibitor for API 5L X-52 steel in 2 M HCl solution using potentiodynamic polarization method. Moxifloxacin is a fluoroquinolones antibiotic. It's commercial name is 7-[-octahydropyrrolo(3,4-6)pyridine-6-yl]-1-cyclopropyl-6-fluoro-8-methoxy-4-oxoquinoline-3-carboxylic acid. The structure of moxifloxacin is presented in Fig. 1.

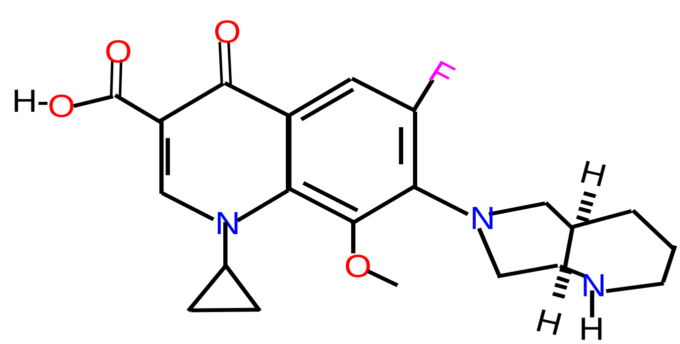

Fig. 1. Chemical Molecular Structure of moxifloxacin

2. EXPERIMENTAL

2. 1. Inhibitor

The Tablets of moxifloxacin were obtained from peace land pharmaceutical shop, Ndidem using iso road, Calabar-Nigeria. And used without further purification. Difference concentrations of the drug were prepared by dissolving appropriate quantities of the Tablets in 10:1 ratio of water : ethanol. From the mass of the drugs sample and it's (Akpan and Offiong, 2014a)

2. 2. Corrosive medium

The corrosive solution was prepared from reagent grade of HCl by dilution using distilled water without further purification in the concentration of 2 Molar.

2. 3. API 5L X-52 Steel specime

The chemical composition of the working electrode API 5L X-52 electrode was determine as (wt %: C = 0.24, Mn = 1.40, P = 0.05, S = 0.015, Si = 0.45, V = 0.01, N = 0.05, Ti = 0.04 and Fe = 97.68).The steel was mechanically polish with a polishing machine using 800, 1200 and 220 emery grade paper. Washed in acetone and distilled water, dried and then used for the experiment.

2. 4. Potentiodynamic polarization measurement

Polarization experiments were carried out in a conventional three electrode cell with a platinum electrode (1 cm^2), a saturated calomel electrode (SCE) couple to a fine capillary as the reference electrode and working electrode. The working electrode was in the form of a square cut (1 cm^2) from API 5L X-52 Steel in epoxy resin of polytetrafluoroethylene (PTFE). The measurement were carried out using a Gamry instrument potentiostat (VFP6.03) DC 105 for polarization measurements, the data were analyzed by Echem Analyst software. the working electrode was immersed in the test solution until a steady state was reached (20 min). The potential was scanned at a scan rate of 0.5 mVs^{-1}. The potential change automatically from –250 to +250 mV (SCE) (Fouda *et al.*, 2013).

3. RESULTS AND DISCUSSION

3. 1. Potentiodynamic polarization

Potentiodynamic polarization curves for corrosion of API 5L X-52 steel in 2M HCl solution in the absence and presence of difference concentration of moxifloxacin at 303K, 313 K and 323 K. is shown in Fig. 1-3. The corrosion current density I_{corr}, anodic(β_a) and cathodic (β_c) Tafel slopes were calculated by extrapolation of linear part of anodic and cathodic curves (Fig 1-3) to the corresponding corrosion potential E_{corr}. The percentage inhibition efficiency (IE%) and degree of surface coverage (θ) were calculated from equ.1

$$IE\% = \theta \ X \, 100 \ = \frac{Icorr\ bl - \ Icorrihb}{Icorrbl} \ X \ 100 \qquad 1$$

The electrochemical parameters evaluated from Tafel polarization curves are summarized in Table 1 and results revealed that the corrosion current density decreased in the presence of moxifloxacin and the inhibition efficiency increased with increasing concentration of moxifloxacin this indicated that moxifloxacin molecules are adsorbed on the metal surface.

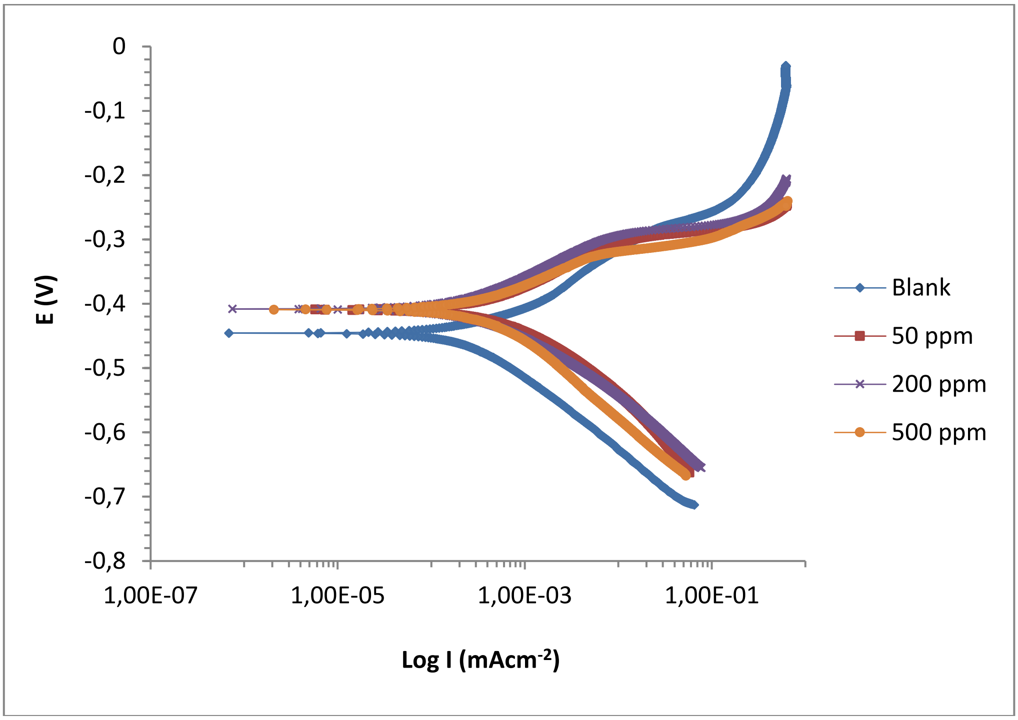

Figure 1. Polarization curves of the corrosion of API 5L X-52 steel in 2 M HCl solution in theabsence and presnce of moxifloxacin (MOXI) at 303 K

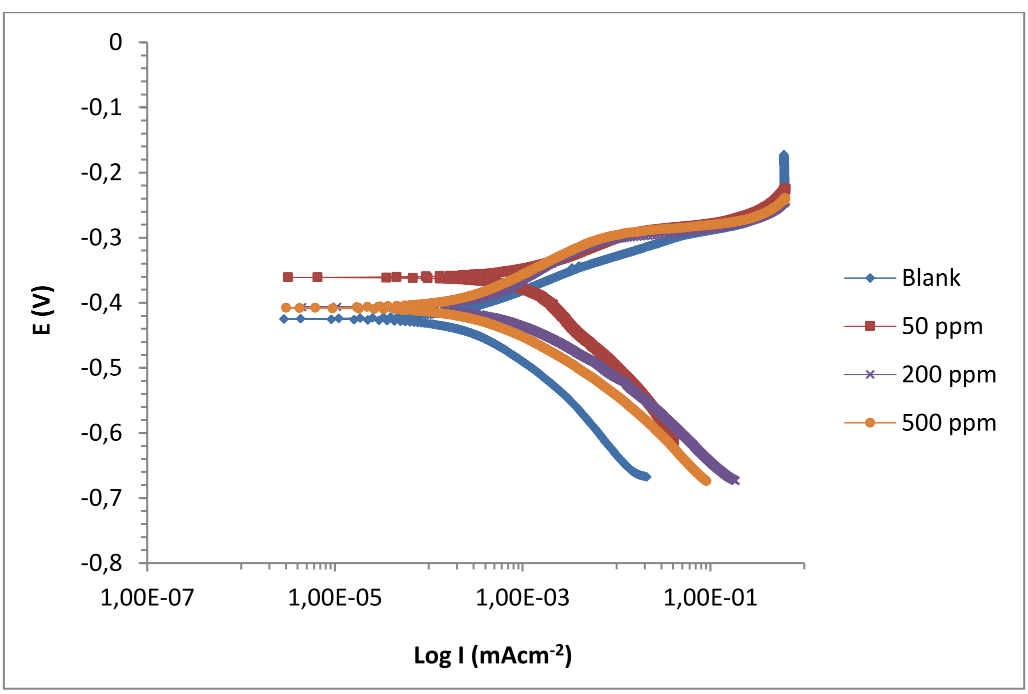

Figure 2. Polarization curves of the corrosion of API 5L X-52 steel in 2 M HCl solution in the absence and presnce of moxifloxacin (MOXI) at 313 K

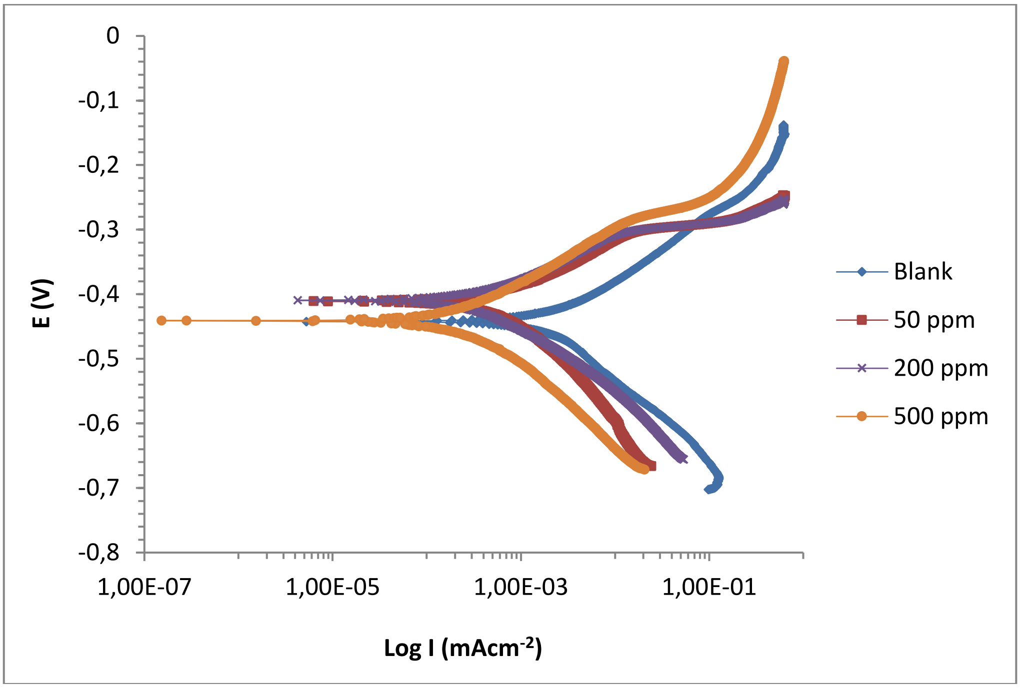

Figure 3. Polarization curves of the corrosion of API 5L X-52 steel in 2 M HCl solution in theabsence and presnce of moxifloxacin (MOXI) at 323 K

Table 1. Parameters obtained from potentiodynamic polarization measurement of API 5L X-52 steel in 2M HCl solution in the presence and absence of difference concentration of moxifloxacin at 303, 313 and 323 K.

Tem. (K)	Conc.	βa $Vdec^{-1}$	βc$Vdec^{-1}$	Ecorr (V)	Icorr (μAcm^{-2})	θ	IE (%)
	Blank	102	254	-446	560		
303	50ppm	83	85	-409	433	0.2267	22.67
	200ppm	76	73	-408	233	0.5839	58.39
	500ppm	61	89	-406	80	0.8571	85.71
	Blank	40	323	-316	1830		
313	50ppm	80	82	-443	1350	0.2610	26.1
	200ppm	65	79	-436	410	0.7131	71.31
	500ppm	68	85	-436	352	0.8661	86.61
	Blank	116	217	-442	3560		
323	50ppm	80	154	-411	690	0.8061	80.61
	200ppm	72	99	-409	392	0.8898	88.98
	500ppm	65	57	-441	84	0.9763	97.63

3. 2. Adsorption isotherm and thermodynamic parameters

The basic information on the interaction between the surface of API 5L X-52 steel and inhibitor can be determined from several adsorption isotherm. The commonly used adsorption isotherms are Langmuir, Tempkin, Frumkin and Flory Huggins isotherms.

The degree of surface coverage (θ) for difference concentration of the inhibitor has be evaluated the data were tested graphically to determined a suitable adsorption isotherm and the experimental data fitted Langmuir adsorption isotherm, Fig. 4.

Illustrated, that adsorption of the inhibitor on the steel surface obeyed Langmuir adsorption isotherm, the negative values of free energy (ΔG_{ads}) indicated spontaneity of a reaction and were obtained from equ. 3. According to the Langmuir adsorption isotherm, the surface coverage (θ) is related to inhibitor concentration by equ. 2 (Ogoko and Ogunsipe, 2015)

$$\log C/\theta = \log C + \log K_{ads} \qquad 2$$

$$\Delta Gads = -2.303\, RT\, Log\, 55.5 Kads \qquad 3$$

where K_{ads} is the equilibrium constant obtained from Fig. 4, R is the gas constant, T is the temperature in Kelvin and 55.5 is the concentration of water.

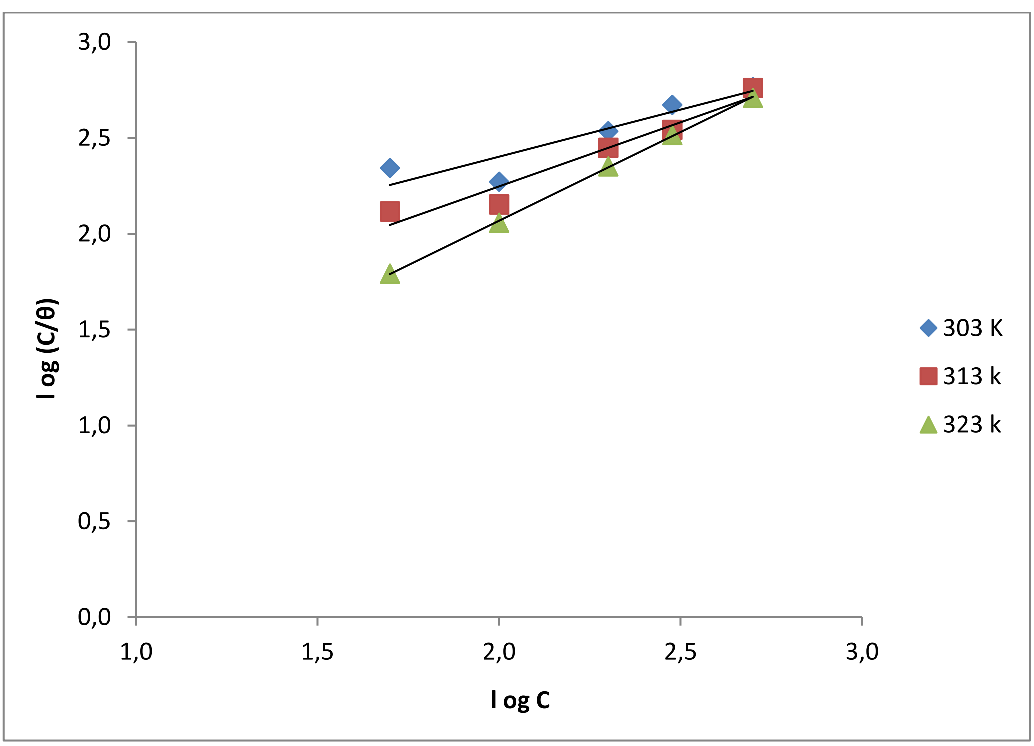

Figure 4. Langmuir Adsorption isotherm of moxifloxacin on API 5L X-52 steel in 2M HCl at different temperature.

Table 4. Thermodynamic parameters of the adsorption of moxifloxacin on API 5L X-52 steel in 2 M HCl at different temperature.

Temperature	$\log_{Kads}$	R^2	ΔG^0_{ads} $KJmol^{-1}$
303 K	1.419	0.847	-18.35
313 K	0.903	0.942	-15.90
323 K	0.216	0.999	-12.12

3. 3. Effect of temperature

The effects of temperature on the corrosion inhibition efficiency (% IE) of API 5L X-52 steel in the presence of various concentration of the inhibitor is presented in Fig. 5. The results from the Fig. 5 show that inhibition efficiency (% E) increased with increasing in temperature which indicated that the there is a stable film formation cause by the adsorbed inhibitor molecules on the steel surface at higher temperature. The apparent activation energy E_a, is formulated as equ. 4.

$$Log\ CR = Log\ A - \frac{Ea}{2.303RT} \quad (4)$$

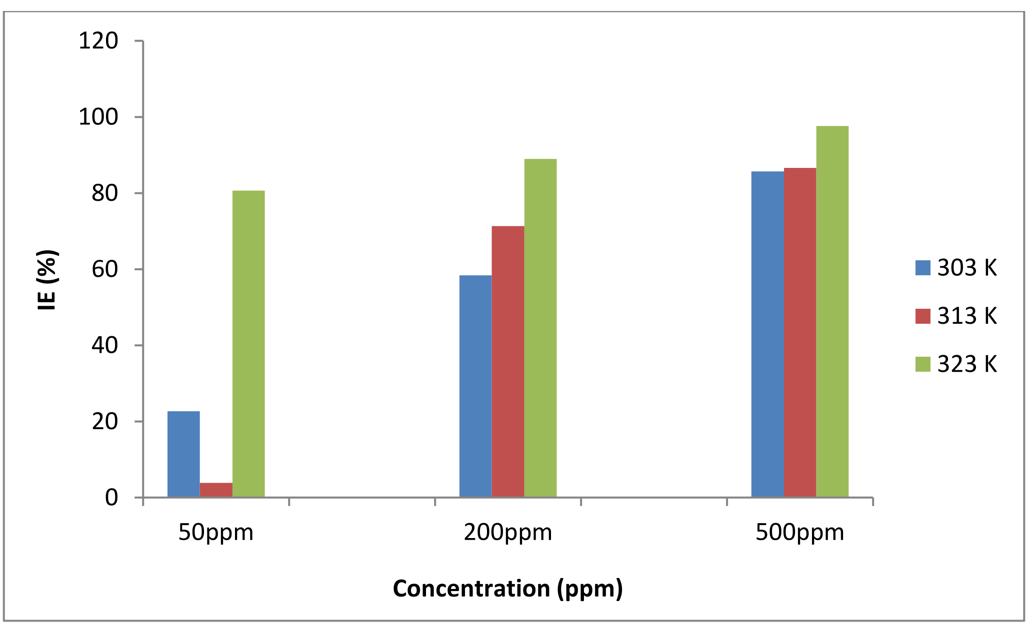

Figure 5. Effect of temperature on %IE of API 5LX-52 steel in 2M HCl in the presence of various concentration moxifloxacin.

Fig. 6 show the Arrhenius plot of log CR against 1/T for the corrosion of API 5L X-52 steel in 2 M HCl solution in the absence and presence of various concentration of inhibitor.

The values of E_a were calculated from the slope of each individual line in Fig. 6 and then listed in Table 5. The E_a values for the inhibited solution were less than for uninhibited solution, suggesting a chemisorptions. The decrease in E_a can be attributed to an increase in the adsorption of the inhibitor molecules on the steel surface with increase in temperature. Similar behavior was previously reported (Singh and Ebenso, 2012). The transition state equation was used to calculated some thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) for the adsorption of moxifloxacin on the mild steel surface. while the quantity of heat adsorbed (Q_{ads}) were calculated from equ. 5 and listed in Table 5.

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \qquad 4$$

$$Qads = 2.303R \left[log\left(\frac{\theta 2}{1-\theta 2}\right) - log\left(\frac{\theta 1}{1-\theta 1}\right) \right] X \left(\frac{T1\ X\ T2}{T2-T1}\right) \qquad 5$$

The positive values of ΔH_{ads} and ΔS_{ads} for the corrosion of API 5L X-52 steel in the presence and absence of the inhibitor reflect endothermic nature of the dissolution process and spontaneous on the reaction respectively. This indicates randomness while moving from reactants to the activated complex as reported (Singh and Ebenso, 2011).

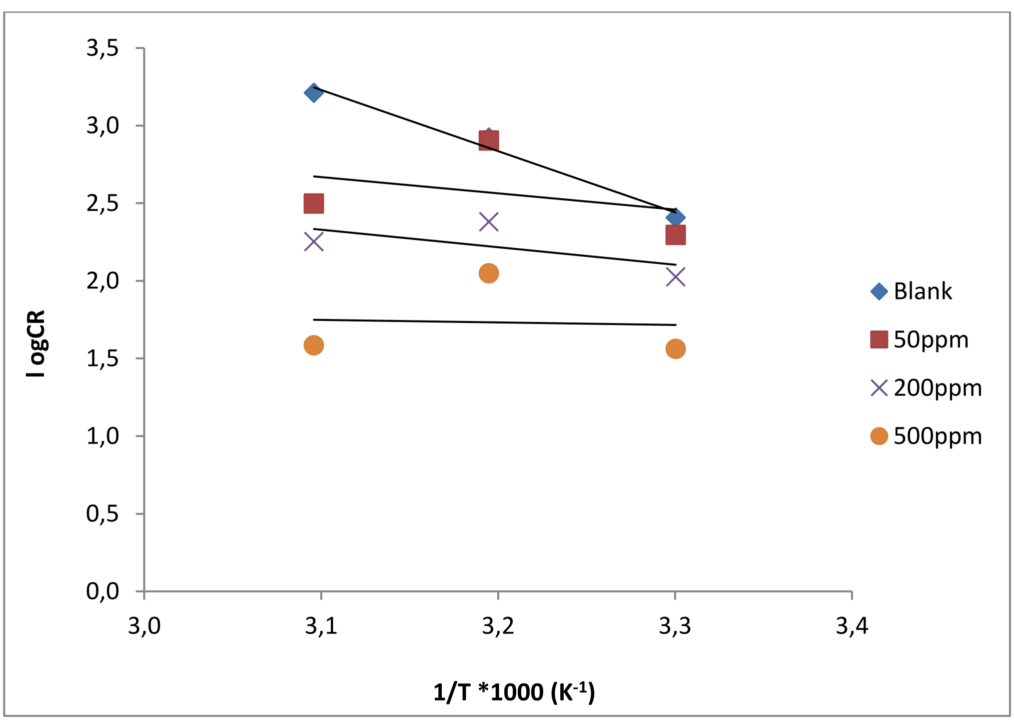

Figure 6. log CR vs 1/T curve for the corrosion of API 5LX-52 steel in 2M HCl in the absence and presence of various concentration moxifloxacin.

Table 5. Kinetics and thermodynamic parameters for API 5L X-52 steel corrosion in 2 M HCl in the absence and presence of various concentration of Moxifloxacin.

Con. PPM	E_a kjmol^{-1}	ΔH_{ads} kjmol^{-1}	ΔS_{ads} kjmol^{-1}	Q_{ads}kjmol^{-1}
Blank	75.45	72.87	239.72	
50ppm	20.04	17.44	57.13	108.04
200ppm	21.59	18.99	55.46	70.85
500ppm	3.1	0.49	12.98	77.91

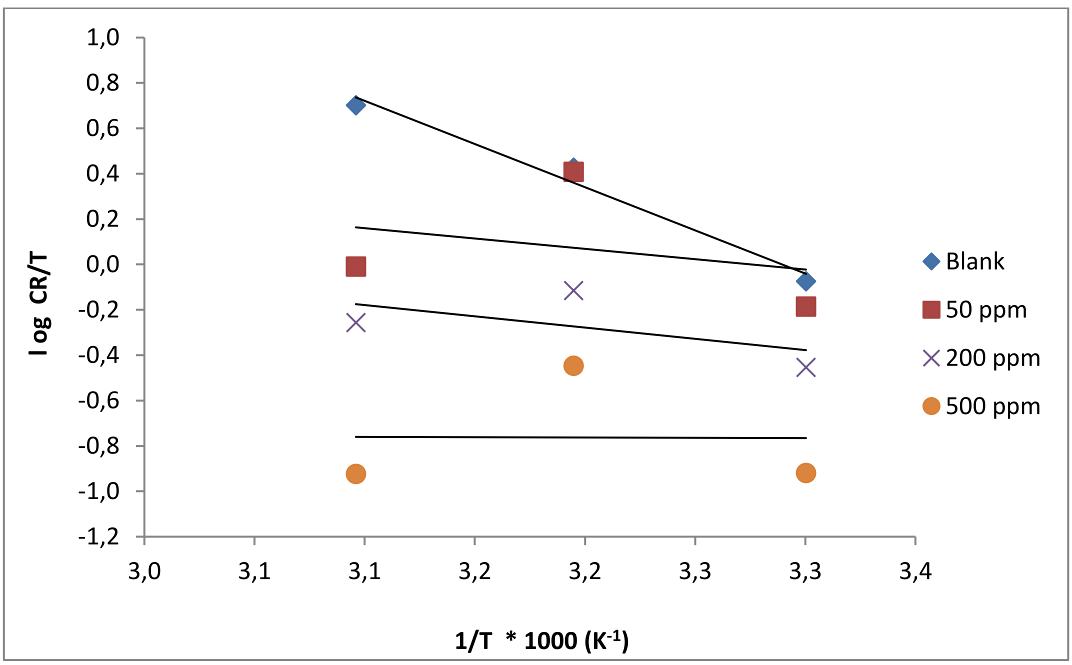

Figure 7. log CR/T vs 1/T curve for the corrosion of API 5L X-52 steel in 2 M HCl in the absence and presence of various concentration moxifloxacin.

4. CONCLUSIONS

1) The investigated drugs was found to perfume well as corrosion inhibitor in aqueous solution at high temperature.
2) The inhibition efficiency increases with increase in the concentration and temperature, which leads to the decrease in activation of the corrosion processes
3) The ΔG_{ads} values indicates a strong and spontaneous adsorption of moxifloxacin on the metal surface.

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