

Temperature effects on the corrosion inhibition of carbon steel in 1M HCl solution by methanolic extract of *Euphorbia Falcata.L*

A. El bribri ^{1,2}, M. Tabyaoui ^{1,*}, H. El Attari ², K. Boumhara ¹,
M. Siniti ³, B. Tabyaoui ¹

¹Laboratoire de Chimie Organique Bioorganique et Environnement, Université Chouaib Doukkali, Faculté des Sciences, BP: 20, Route Ben Maachou 24000 El Jadida, Morocco

²Laboratoire de Chimie de Coordination et d'Analytique, Université Chouaib Doukkali, Faculté des Sciences, BP: 20, Route Ben Maachou 24000 El Jadida, Morocco

³Laboratoire de Chimie Physique, Université Chouaib Doukkali, Faculté des Sciences, BP: 20, Route Ben Maachou 24000 El Jadida, Morocco

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*Corresponding author, Email: hamidtabyaoui@yahoo.fr, Tel. +212 661 749 041, Fax. +212 523 342 187,

Abstract

Gravimetric method was used to study the temperature effects on carbon steel corrosion in molar HCl solution, in the absence and presence of methanolic extract of *Euphorbia Falcata.L* (MEEF). The results revealed that the inhibition efficiency of MEEF increased with the inhibitor concentration. The highest inhibiting efficiency reached 96% at 323 K at 3g/L. The adsorption was spontaneous and followed Langmuir adsorption isotherm at all studied temperatures. Thermodynamic data for inhibitor adsorption and carbon steel corrosion lead to suggest the manner of the adsorption of MEEF.

Key words: Corrosion; euphorbia; inhibition; carbon steel; gravimetric; adsorption

1. Introduction

The use of inhibitors is one of the best options of protecting metals against corrosion [1-10]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful uses of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups [11-28].

Temperature dependence of the inhibitor efficiency (IE) and the comparison of the obtained thermodynamic data of the corrosion process both in absence and presence of inhibitors lead to some conclusions concerning the mechanism of inhibiting action [29-30].

The present work aimed to study the temperature effects on carbon steel corrosion in molar HCl solution in the absence and presence of various concentrations of methanolic extract of *Euphorbia Falcata.L* (MEEF) by using gravimetric method. Various thermodynamic parameters for inhibitor adsorption on carbon steel surface were estimated and discussed. Kinetic parameters for carbon steel corrosion in absence and presence of the studied inhibitors were evaluated and interpreted.

2. Experimental detail

Thin plates (C: 0.21, Mn: 0.05, Si: 0.38, S: 0.05, P: 0.09, Al: 0.01 and the remainder iron) were used. Prior to each experiment, the carbon steel specimen was abraded with a series of emery paper from 400 to 1500 grades. The specimen was washed several times with distilled water then with ethanol and finally dried using a stream of air.

The acidic solution 1M HCl was prepared by dilution of Analytical Grade 37% HCl with distilled water.

The aerial part of *Euphorbia Falcata.L* was collected in June 2008 in the region of El Jadida (Morocco). A specimen was put down in the herbarium of the Faculty of Science El jadida (Morocco). The dried plant material is stored in the laboratory at room temperature (298 K) before extraction.

The inhibitor material (MEEF) is prepared by refluxing aerial parts of *Euphorbia Falcata.L*, in absolute methanol, for 4 hours, then filtered and the solvent is removed to lead extract.

Gravimetric methods are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 30 ml. The steel specimens used have rectangular shapes 3.5cm×1cm×0.1cm. For each sample, three tests are realized and the corresponding average value is calculated. The samples were weighted with an uncertainty of 10^{-4} g. The immersion time for weight loss amounts is 6h for all the temperatures.

3. Results and discussion

3.1. Effect of temperature on mild steel corrosion rates

The corrosion rate “w” was calculated from the following equation (1).

$$w = \frac{m_1 - m_2}{s.t} \quad (1)$$

m_1 (mg) and m_2 (mg) are the masses of the specimen before and after corrosion, S (cm²) is the total area of the specimen and t (h) is the immersion time.

The weight loss data made at 6 hours of immersion are given in Table 1.

Table 1: Corrosion rates of mild steel specimen in 1M HCl in the absence and presence of different concentrations of MEEF at different temperatures.

w (mg.cm ⁻² .h ⁻¹)						
T(K)	0.0 g/L	0.6 g/L	1.2 g/L	1.8 g/L	2.4 g/L	3.0 g/L
298	0.295	0.083	0.067	0.062	0.057	0.045
313	3.062	1.198	0.819	0.593	0.498	0.114
323	6.388	2.452	1.900	1.848	1.405	0.245
333	11.898	4.640	3.388	3.202	2.512	0.562
343	16.898	8.786	7.045	6.090	5.162	0.924

As observed in Table 1, a remarkable decrease in the carbon steel corrosion rate was observed with the addition of increasing amount of MEEF at each studied temperature.

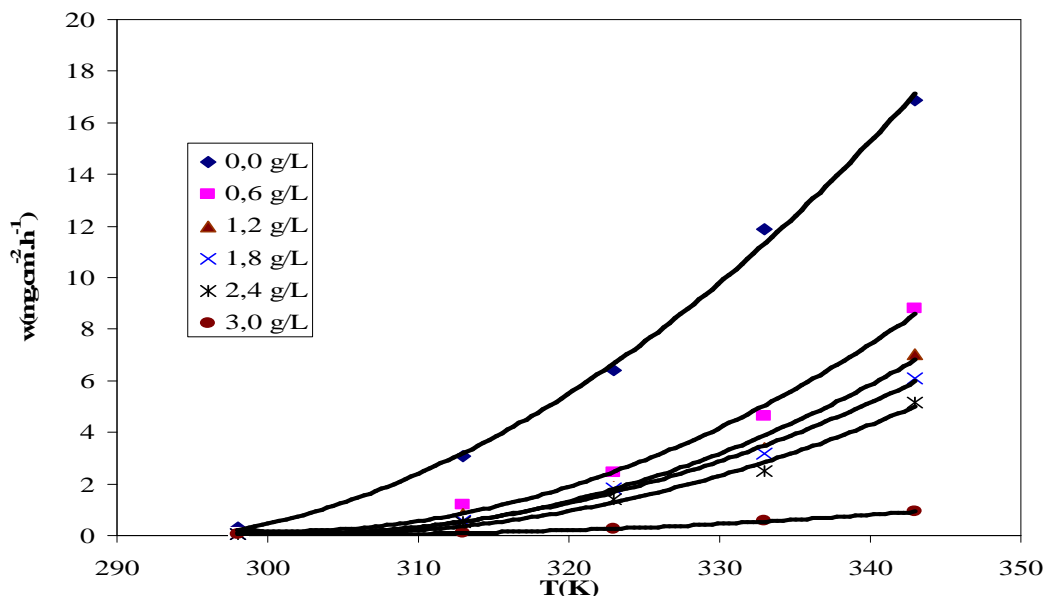


Figure 1: Corrosion rates w ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) of carbon steel specimen in 1MHCl at different concentrations

It is clear from Table1 that the corrosion rate of carbon steel in acid medium in absence and presence of MEEF obeys to the Arrhenius type reactions as it increases with the rising solution temperature.

3.2. Effects of temperature on inhibition efficiency IE (%)

The inhibition efficiency IE (%) for the carbon steel corrosion in acidic medium in the presence of various concentrations of MEEF and at temperature of 298 K to 343 K was obtained from the following equation:

$$IE = \left(\frac{w_{corr}^{\circ} - w_{corr}}{w_{corr}^{\circ}} \cdot 100 \right) \tag{2}$$

w_{corr}° and w_{corr} are the corrosion rates of carbon steel in absence and presence of concentration of MEEF, respectively.

The obtained data in Table 2 reveal that, the inhibition efficiency increased with an increase in the inhibitor concentration. The highest inhibiting efficiency reached 96% at 323 K at 3g/L.

Table 2: Inhibition efficiencies of MEEF at different concentrations and temperatures in 1M HCl

$IE(\%)$					
$C_{inh}(\text{g/L})$	298 K	313 K	323 K	333 K	343 K
0.6	72	61	62	61	48
1.2	78	73	70	72	60
1.8	80	81	71	73	64
2.4	81	84	80	80	70
3.0	85	96	96	95	95

As observed from Table 2 and Figure 2, the effect of temperature on the inhibition efficiency of the studied inhibitor at all concentrations and temperatures shows that: in 1M HCl solutions, the inhibition corrosion increases with the inhibitor concentration. The inhibitory effect stops to jump from 96% at 323 K.

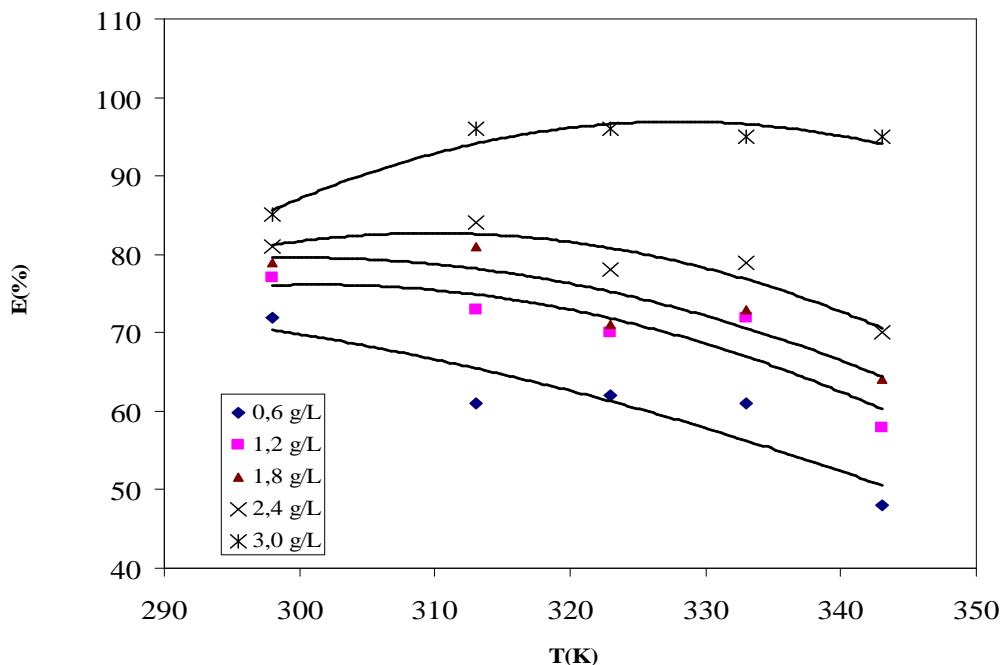
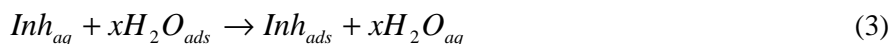


Figure 2: Variation of *IE* (%) with MEEF concentration at different temperatures in 1M HCl

3.3. Parameters of adsorption

3.3.1. Adsorption isotherms

In the acid environments, the inhibitors act at first by adsorption on the surface of metals before intervening in the reaction processes of corrosion to decrease the speed. The phenomenon of adsorption is made according to equation (3):



when the equilibrium of the process described in equation (3) is reached, it is possible to obtain different expressions of the adsorption isotherm plots. The degree of surface coverage θ can be plotted as a function of the concentration of the inhibitor under test [31] in 1M HCl. Langmuir mathematical expressions is given as follow (4):

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad \text{with} \quad K_{ads} = \frac{1}{C_{H_2O}} \exp\left(-\frac{\Delta G_{ads}^\circ}{RT}\right) \quad (4)$$

where C_{inh} is the concentration of the inhibitor, K_{ads} is the adsorptive equilibrium constant; θ is the surface coverage and the standard adsorption free energy ΔG_{ads}° . The relationship between $\frac{C_{inh}}{\theta}$ and C_{inh} presents linear behaviours at all temperatures (figure 3) with slopes equal to unity. For this reason Langmuir adsorption isotherm was preferred to fit the results.

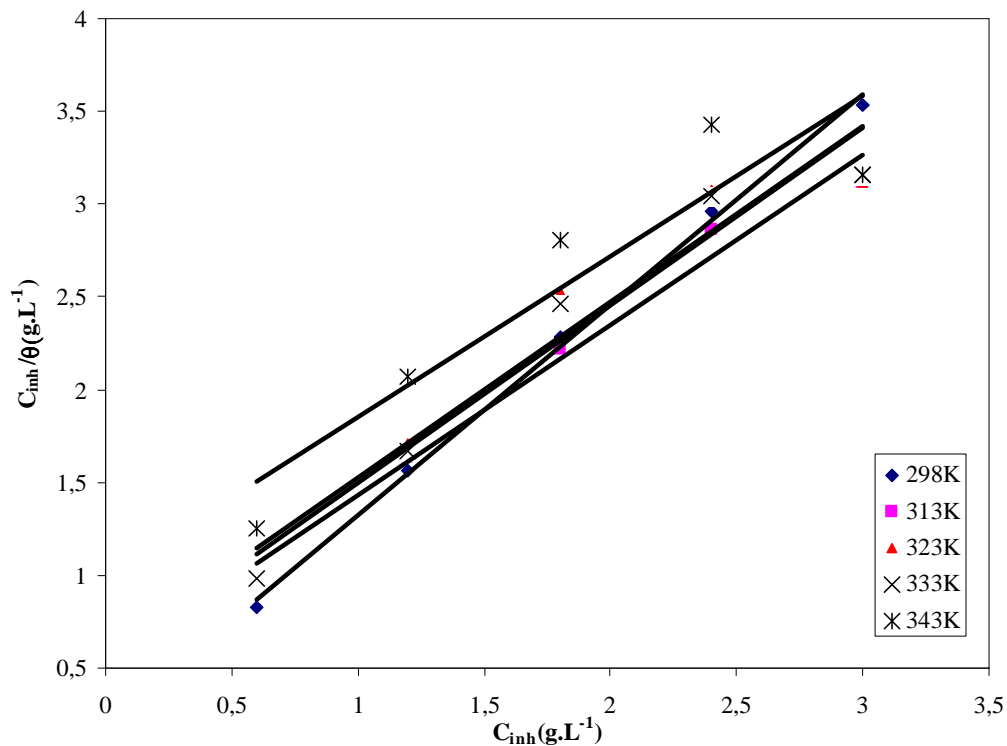


Figure 3: Langmuir adsorption isotherm of MEEF on carbon steel surface in 1M HCl

3.3.2. Thermodynamic adsorption parameters

The ΔG_{ads}° values at all studied temperature can be calculated from the following equation (5):

$$\Delta G_{ads}^\circ = -RTLn(C_{H_2O} \cdot K_{ads}) \tag{5}$$

In equation (5), we use C_{H_2O} in g/L (10^3 g/L) and K_{ads} in L/g, the unity of ΔG_{ads}° depends only on the factor RT (kJ.mol^{-1}). The obtained values are summarized in table 3.

Table 3: The variation of ΔG_{ads}° versus T (K) in 1M HCl

T(K)	K_{ads} ($\text{g}^{-1} \cdot \text{L}$)	ΔG_{ads}° (kJ.mol^{-1})
298	5.20	- 21.05
313	1.94	- 19.80
323	1.72	- 20.00
333	1.80	- 20.70
343	1.16	- 19.60

ΔH_{ads}° and ΔS_{ads}° are obtained from the following equation [32]:

$$\Delta G_{ads}^\circ = \Delta H_{ads}^\circ - T\Delta S_{ads}^\circ \tag{6}$$

Figure 4 shows the variation of ΔG_{ads}° versus T. A straight line is obtained. The slope gives ΔS_{ads}° and the intercept leads to ΔH_{ads}° . The obtained values are given in table 4.

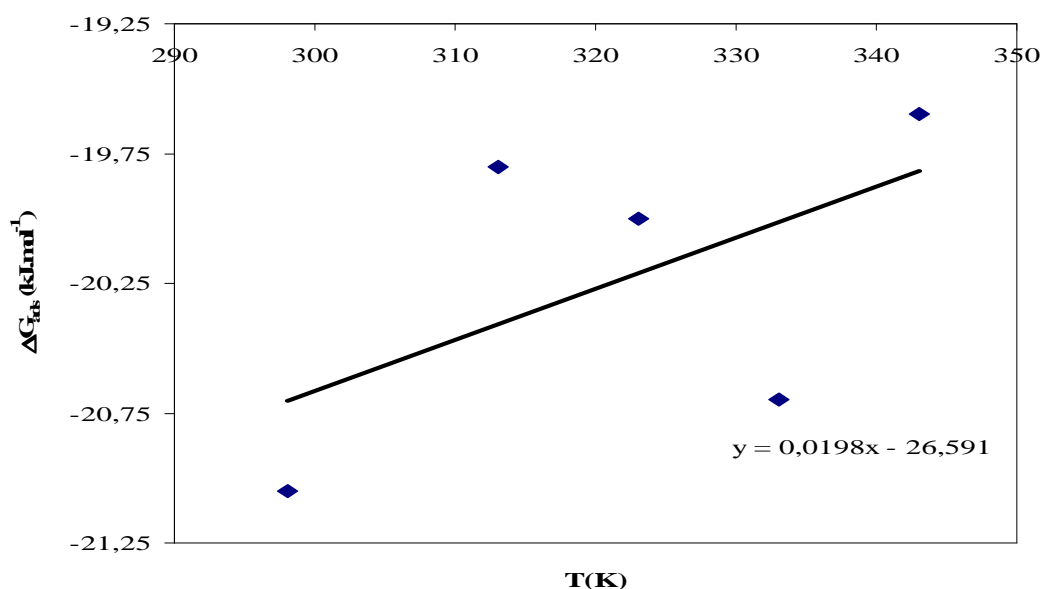


Figure 4: The variation of ΔG_{ads}° versus T (K) in 1M HCl

Table 4: Thermodynamic parameters for the adsorption of MEEF on mild carbon in 1M HCl at different temperatures.

T (K)	ΔG_{ads}° (kJ.mol ⁻¹)	ΔH_{ads}° (kJ.mol ⁻¹)	ΔS_{ads}° (kJ.mol ⁻¹ K ⁻¹)
298	- 21.05	- 26.59	-0.018
313	- 19.80		-0.022
323	- 20.00		-0.020
333	- 20.70		-0.018
343	- 19.60		-0.020

The adsorption parameters gathered in Table 4, enable to clarify the interaction of natural extract compound with the metallic surface.

In general, two kinds of adsorption can be considered; physical adsorption or chemical adsorption and sometimes both of these kinds [1]. The negative values of ΔH_{ads}° indicate that the adsorption of inhibitor is an exothermic process [32]. The literature pointed out that an exothermic process means either physisorption or chemisorptions, while an endothermic process is associated to chemisorption [33]. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of a physisorption process. In physisorption, the values are lower than 40 kJ mol⁻¹ while the adsorption heat of a chemisorption process approaches 100 kJ mol⁻¹ [34]. In the molar HCl solution, an exothermic adsorption was detected. The average value ΔH_{ads}° obtained is about -26.59 kJ.mol⁻¹ and reinforces that a comprehensive adsorption

(physical adsorption) might occur. The adsorption of inhibitor molecules is accompanied by negative values of ΔS_{ads}° . It might be explained by an ordered layer onto the steel surface.

The values of ΔG_{ads}° were negative at the studied temperatures, which indicates that the adsorption process of MEEF occurs spontaneously.

The inhibition of the metal corrosion is due to the electrostatic interaction between the charged molecules of MEEF and the charged metal (physisorption); those around -40 kJ.mol^{-1} or higher involve charge sharing from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [35-36]. The estimated ΔG_{ads}° values oscillating around -20 kJ.mol^{-1} indicate that the adsorption mechanism of the MEEF tested may be a physisorption type.

3.4. Kinetic-thermodynamic corrosion parameters

As noticed previously, the adsorption process was well elucidated by using a thermodynamic model. In addition, a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor.

The apparent effective activation energies (E_a) for the corrosion reaction of carbon steel in HCl, in the absence and presence of different concentrations of MEEF were calculated from Arrhenius-type equation:

$$\log w_{corr} = \log A - \frac{E_a}{2,303.RT} \tag{7}$$

where A is the Arrhenius pre-exponential factor. The plots of $\log(w_{corr})$ versus $1/T$ gave straight lines as shown in Figure 5.

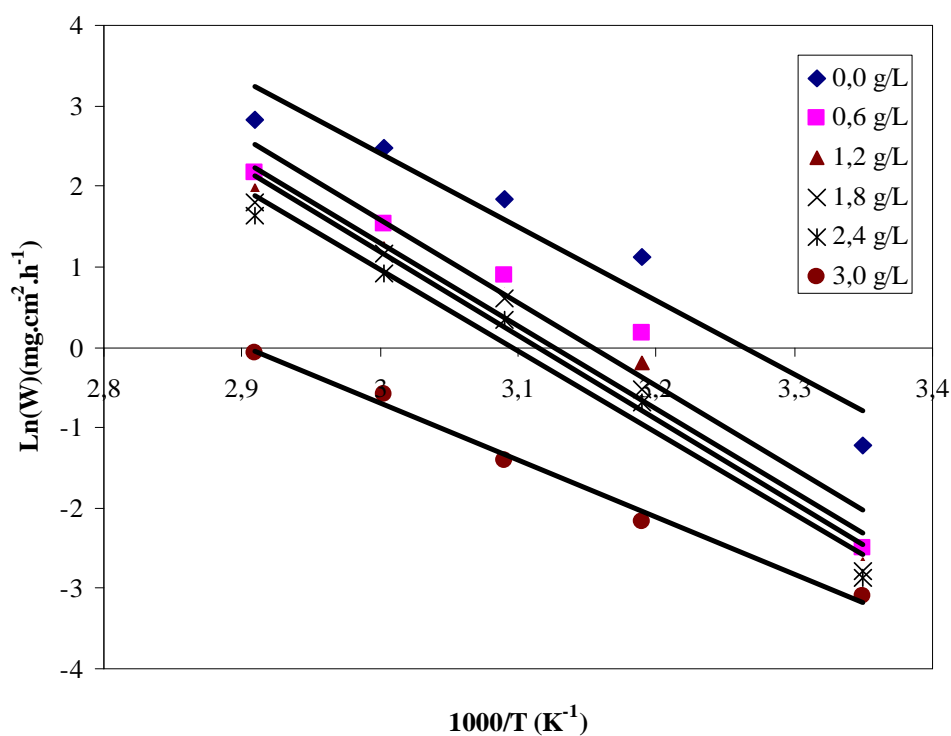


Figure 5: Arrhenius plots for carbon steel corrosion rates (w_{corr}) in 1 M HCl, in absence and presence of various concentrations of MEEF

The variation of the apparent activation energy E_a in the absence and presence of inhibitor is largely discussed in the literature [2-4, 29, 37-38]. It reported that values of E_a increase or decrease in the presence of inhibitor.

The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the intermediate complex in the transition state for the corrosion of carbon steel in HCl, in the absence and presence of different concentrations of MEEF were obtained by applying the transition state equation [39]:

$$\log\left(\frac{w_{corr}}{T}\right) = \left[\log\left(\frac{R}{hN}\right) + \frac{\Delta S^*}{2,303R} \right] - \frac{\Delta H^*}{2,303RT} \tag{8}$$

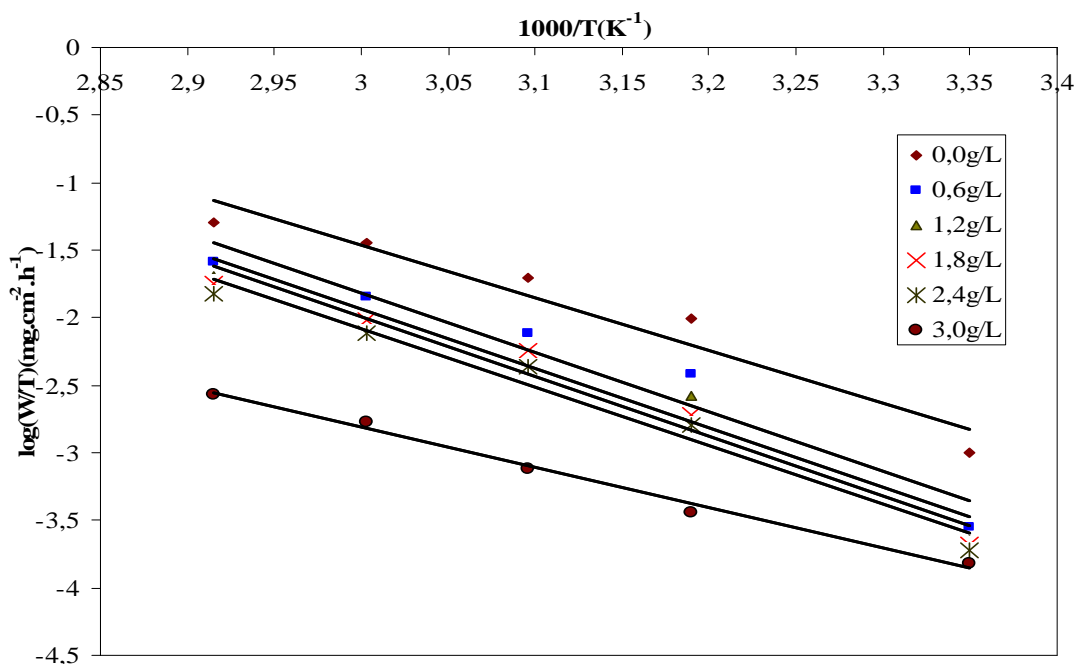


Figure 6: Transition-state plots for carbon steel corrosion rates in 1 M HCl in absence and presence of various concentrations of MEEF.

The variation of $\log\left(\frac{w_{corr}}{T}\right)$ according to the opposite of the temperature is a right (figure.5), with a slope of

$(\Delta H^*/R)$ and an intercept equal to $\left(\log\left(\frac{R}{hN}\right) + \frac{\Delta S^*}{R}\right)$. We can calculate the values of ΔH^* and ΔS^* . These

values are recorded in Table 5.

Table 5: Kinetic-thermodynamic corrosion parameters for carbon steel corrosion in absence and presence of various concentrations of MEEF, in 1M HCl

$C_{inh}(g/L)$	$E_a(kJ.mol^{-1})$	$\Delta H^*(kJ.mol^{-1})$	$\Delta S^*(kJ.mol^{-1}.K^{-1})$
0.0	74.13	74.40	0.408
0.6	84.16	83.96	0.020
1.2	83.95	84.05	0.018
1.8	84.68	84.58	0.018
2.4	83.8	82.76	0.011
3.0	58.38	56.97	-0.080

The values of E_a are superior to the value of the white. They are of the order of 84 kJ.mol^{-1} except for 3 g/L, E_a is lower than that of the white ($58.38 \text{ kJ.mol}^{-1}$), and the efficiency is 95 %. When E_a in the presence of the inhibitor is superior to the value of the white, this phenomenon is generally interpreted as consequence of the physisorption. For 3 g/L, this phenomenon is interpreted by the chemisorption.

Conclusion

* In 1M HCl, the inhibition efficiency of MEEF increases with increasing concentration to reach 96% at 3 g/L.

* The inhibition action of MEEF is performed via adsorption of the extract species on carbon steel surface. The adsorption is spontaneous.

* Thermodynamic data for the inhibitor adsorption lead to suggest the occurrence may be a physical adsorption

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