Synthesis and anticorrosive effects of epoxy-allylpulegols on steel in molar hydrochloric acid

L. Majidi [1*], Z. Faska [1], M. Znini [1], S. Kharchouf [1], A. Bouyanzer [2], B. Hammouti [2]

[1] *Laboratoire des Substances Naturelles & Synthèse et Dynamique Moléculaire, Faculté des Sciences et Techniques, Université Moulay Ismail, Errachidia, Morocco.*
[2] *LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco.*

Received in 27 Sept 2010, Revised 28 Nov 2010, Accepted 29 Nov 2010.

*Corresponding author. Tel. +212 53 55 74 497; Fax. +212 53 55 74 485; e-mail: lmajidi@yahoo.fr

Abstract- Allylpulegols **(2-4)** and epoxy-allylpulegols **(5-7)** are synthesised from R-(+)pulegone, the major compound of Mentha pulegium oil. The compounds (**2-7**) are tested as corrosion inhibitors of steel in 1M HCl using weight loss measurements. The addition of allylpulegols decreases weakly the corrosion rate, but in the presence of epoxy-allylpulegols the corrosiveness of acid is reduced. Epoxy-allylpulegols tested adsorb on the steel surface according to Langmuir isotherm. The negative values of free enthalpy indicate that these compounds act spontaneously on the metal surface. The higher inhibition efficiency (79 %) is obtained for **5** at 0.8 g/L at one hour of immersion. The corrosion rate decreases with rise of temperature in the presence and absence of inhibitors. The corresponding efficiency decreases with the temperature. The corresponding activation energies are determined.

*Keywords***:** Corrosion, Inhibition, Steel, Pulegone, allylpulegols, epoxyallylpulegols, Adsorption

1. Introduction

The toxic effect of most synthetic organic compounds us as corrosion inhibitors reoriented researchers to find new alternative of naturally occurring, environmentally friendly, inexpensive, readily available and renewable sources of materials. Plant extracts and oils as well as natural compounds become more and more environmentally acceptable. The use of natural substances will establish both the economic and environmental goals. Plant extracts and oils constitute a rich source of naturally synthesized chemical compounds that can be extracted and purified with low cost. Plant extract was found to reduce the corrosion of steel more effectively in acidic media [1-525]. Inhibition of metals may be occurred by natural compounds such as aminoacids, aminoesters, peptides and their derivatives [6-11]. Many researchers examined various naturally occurring substances as corrosion inhibitors for different metals in various environments, we cite honey, henna, Opuntia, Guar Gum, Lawsonia, ananas, bauhinia purpurea… [11–16].

Detailed analysis of essential oils composition shows that they contain remarkable amounts of organic compounds containing p-menthene carbon skeleton. On the other hand, it has been shown that the widespread occurrence of p-menthane system in many classes of natural products have made them valuable building block for the synthesis of various biologically organic target molecules [17]. We previously reported that pure compounds issued from medicinal and aromatic plants have been found to be very efficient corrosion inhibitors for steel in acid media [18-23]. Thus, Synthesis of various p-menthane derivatives was extensively studied with the goal to obtain biologically active compounds. p-menth-4(8)-en-3-one **1** (pulegone) have become the key starting natural compound for the synthesis of a number of substances exhibiting various kinds of biologically activity [24]. Pulegone, a monoterpene ketone, occurs in nature and is widely present in high concentrations in the essential oil of mentha pulegium [25] and other essential oils [26].

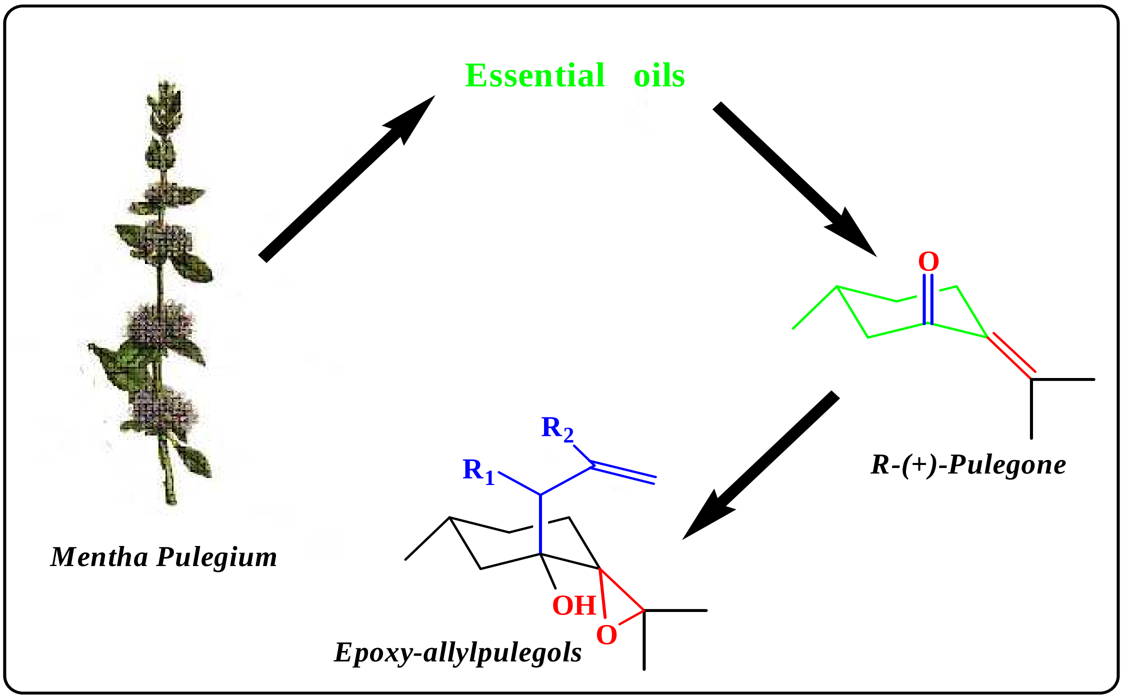
The goal of the present study was to synthesis three allylpulegols and their corresponding epoxy-allylpulegols and to test by gravimetric method, the effect of p-menthene derivatives (allylpulegols) **2-4** and epoxy-allylpulegols **5-8** on the corrosion of steel in 1M HCl solution. Effect of temperature from 308 to 338 K is also studied.

2. Experimental

2.1. Synthesis of inhibitors

Infrared (IR) spectra were recorded on Schimatzu IR-470. ^1H NMR spectra were determined on a Brüker AC250 (250 MHz) spectrometer with Me_4Si as the internal standard. ^{13}C NMR spectra of $CDCl_3$ solution were recorded on Brüker AC250 (60 MHz).
Infrared (IR) spectra were recorded on Schimatzu IR-470. ^1H NMR spectra were determined on a varian XL 200 (200 MHz) spectrometer. ^{13}C NMR spectra of $CDCl_3$ solution were recorded on Varian XL 200 (50.309 MHz) with Me_4Si as the internal standard. Melting points are uncorrected and were obtained on a capillary apparatus.

General procedure for epoxidation of allylpulegols 2-4.
Allylpulegols **2-4** were prepared by condensation of allylic magnesium chloride on pulegone according to the method described in literature [27].



Scheme 1: From Mentha Pulegium to Pulegone derivatives

Dichloromethane solution of m-chloroperbenzoïc acid (15mmol in 20ml of CH_2Cl_2) was added to a solution of allylpulegol (15mmol in 10ml of CH_2Cl_2) in dichloromethane at room temperature. The reaction mixture was steered for four hours and then filtered. The solution was washed successively with 10% Na_2CO_3, 5% $NaSO_3$, and saturated NaCl solution and dried. The solvent was removed and residual oil was chromatographed on silica gel (eluant n-hexane).

- 3-(2,3-epoxypropan-3-yl)-p-mentnan-3-ol **(5, $C_{13}H_{22}O_2$)**:

Yield 75%. ^1H NMR ($CDCl_3$): δ = 5,88 (1H, m), 5,06 (2H, m), 1,63 (3H, s), 1,30 (3H, s), 1,20-2,30 (10H, m), 0,88 (3H, d, J = 5,5 Hz); ^{13}C NMR ($CDCl_3$): δ = 133,6 (d), 117,4 (t), 72,8 (s), 66,7 (q), 63,9 (s), 47,6 (t), 39,7 (t), 31,7 (t), 29,4 (d), 28,2 (t), 23,6 (q), 22,0 (q), 21,7 (q); IR (KBr): ν 3440; 3080; 1635; 1040; 910; 870 cm^{-1}.

- 3-(2,3-epoxy-1-methylpropan-1-yl)-p-menthan-3-ol **(6,** $C_{14}H_{24}O_2$):

Yield 75%. ^1H NMR ($CDCl_3$): δ = 5,92 (1H, m), 5,01 (2H, m), 1,63 (3H, s), 1,20-2,35 (15H, m), 0,88 (3H, d, J = 5,5 Hz); ^{13}C NMR ($CDCl_3$): δ = 140,2 (d), 115,1 (t), 75,3 (s), 69,3 (s), 65,9 (s), 47,3 (t), 41,4 (d), 31,4 (t), 28,8 (d), 27,5 (t), 23,9 (q), 22,9 (q), 21,9 (q), 15,4 (q); IR (KBr): ν = 3480, 3080, 1635, 1035, 960, 890 cm^{-1}.

- 3-(2,3-epoxy-2-methylpropan-1-yl)-p-menthan-3-ol (**7**, $C_{14}H_{24}O_2$)

Yield 75%. ^1H NMR ($CDCl_3$): δ = 4,76 (2H, m), 1,70 (3H, s), 1,25-2,30 (10H, m), 1,53 (3H, s), 1,20 (3H, s), 0,83 (3H, d, J = 5 Hz); IR (KBr): ν = 3480, 3080, 1635, 1035, 960, 890 cm^{-1}

2.2. Gravimetric method

Steel samples (0.21% C, 0.38% Si, 0.09% P, 0.01% Al, 0.05% Mn, 0.05% S) are used. The aggressive solution (1M HCl) is prepared by dilution of Analytical Grade 37% HCl with double distilled water.

Weight loss is measured on sheets of steel of apparent surface area of $5cm^2$. These sheets are abraded successively with fine emery paper until 1200 grade. The sheets are then rinsed with distilled water, degreased and dried before being weighed and immersed in 60 ml of the corrosive medium. The immersion time for the weight loss is 6 hours at room temperature 298 K in air without bubbling in a double walled glass cell equipped with a thermostat-cooling condenser. Each value is the mean of triplicate experiences.

The percent inhibition, E% for the weight loss method, is calculated as follows:

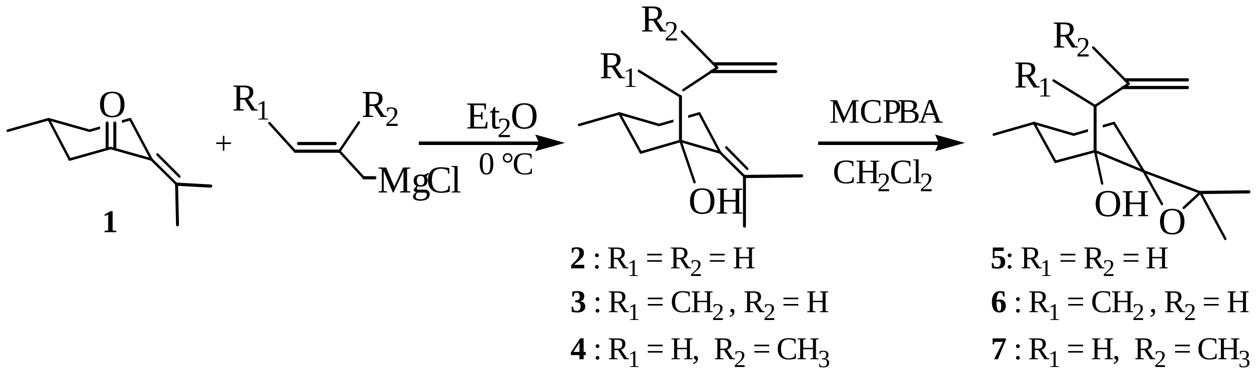
$$E_w\,\% = \frac{W_{corr} - W_{corr\,(inh)}}{W_{corr}} \times 100 \qquad (1)$$

W_{corr} and $W_{corr(inh)}$ are the corrosion rates of steel samples without and with inhibitor, respectively.

3. Results and discussion

3.1. Synthesis of epoxy-allylpulegols 5-7

The treatments of allylpulegols **2**-**4** with m-chloroperbenzoic acid in dichloromethane give regio and stereoselectivelly epoxy-allylpulegols **5**-**7** in good yields. Allylpulegols **2**-**4** were obtained stereospecifically by the condensation of allylic Grignard reagents on pulegone [11] (scheme 2).



Scheme 2

The regio and stereoselectivite epoxidation of allylpulegols are not induced by the hydroxyl group: the utility of hydroxyl group directed epoxidation has been demonstrated in a number of cyclic allylic alcohols. It was suggested that a hydrogen bond formed between the hydroxyl group and peracid leads to delivery the reagent to the face of the double bond syn to hydroxyl group [28]. However, epoxidation of allylic alcohols having exocyclic double bond is not stereoselective. Indeed, the hydroxyl group of cis-pulegol does not significantly direct the approach of peracid as in case of a large number of allylic alcohols reported in the literature [29]. The stereoselectivity epoxidation of allylpulegols is due to steric hindrance: the axial allylic moieties group opposes the approach of peracid to allylpulegols tetra-substituted double bond.

The regioselectivity of peracid on the tetra-substituted double bond of allylpulegols **2**-**4** is determined by a combination of infrared spectra, ^1H NMR and ^{13}C NMR analyses of corresponding epoxy-allylpulegols **5**-**7**. The IR spectra contain a narrow band due to the vinylic protons of allylic moieties ($C=CH_2$ near 3080 cm^{-1}) and a band assigned to the double bond C=C near 1635 cm^{-1}. The ^{1}HNMR spectrum of each product shows that the massifs due to the protons of the allylic moieties remain unaltered. In the ^{13}CNMR spectrum, we noted the absence of the signals attributed to two sp^2 carbons of the tetrasubtituted double bond. However, the signals of both carbons of allylic double bond remained unaltered. This is mainly due to electronic factors; allylic double bond is mono or disubstituted. It is well known that the peracid strongly discriminates in favour of more highly alkylated olefins.

3.2. Gravimetric results

The effect of three allylpulegols **2-4** compounds on the corrosion rates of steel were determined in aerated 1M HCl solution at various concentrations for 6 hours at 298 K. The corrosion rate values and the corresponding inhibition efficiency are summarised in Table 1. A slight decrease in corrosion rate reveals that the tested allylpulegols exhibits a limited inhibitive effect on the corrosion of steel in acid solution. The higher E% observed is 60, 52 and 51% at 0.8 g/l for compounds **2**, **3** and **4**, respectively (Take in Table 1).

Table 1: Influence of allylpulegols **(2-4)** concentration of on the steel corrosion in 1M HCl at 6 hours.

Compounds 2-4	**C (g/l)**	**W (mg/cm^{2}h)**	**E %**
Blank	0.00	0.4524	--
Allylpulegol **2**	0.20	0.3302	27
	0.35	0.2985	34
	0.50	0.2488	45
	0.80	0.1811	60
Allylpulegol **3**	0.20	0.3393	25
	0.35	0.3076	32
	0.50	0.2669	41
	0.80	0.2171	52
Allylpulegol **4**	0.20	0.3438	24
	0.35	0.3122	31
	0.50	0.2624	42
	0.80	0.2217	51

This result has incited us to ameliorate the efficiency by transforming of allylpulegols compounds to their corresponding epoxides **5, 6** and **7**. The change in the molecular structure induced a decrease in the corrosion rate of steel. The best action is observed with 3-(2,3-epoxypropan-1-yl)-p-mentnan-3-ol **5** which leads to 75% at 0.8 g/l (Take in Table 2).

Table 2: Influence of epoxy-allylpulegols **(5-7)** concentration of inhibitor on the steel corrosion in 1M HCl at 6 hours.

Compounds 5-7	**C (g/l)**	**W (mg/cm^{2}h)**	**E %**
Blank	0.00	0.4524	-
Epoxy-allylpulegol **5**	0.20	0.2940	35
	0.35	0.2352	48
	0.50	0.1809	60
	0.65	0.1448	68
	0.80	0.1131	75
Epoxy-allypulegol **6**	0.20	0.3032	33
	0.35	0.2488	45
	0.50	0.2036	55
	0.65	0.1719	62
	0.80	0.1357	70
Epoxy-allylpulegol **7**	0.20	0.3167	30
	0.35	0.2533	44
	0.50	0.2171	52
	0.65	0.1855	59
	0.80	0.1493	67

The corrosion rate of steel with temperature was studied in molar HCl both in the absence and presence of inhibitor at a maximal concentration (0.8 g/l) in the temperature range 303-328 K using weight loss measurements, the corresponding results are summarised in Table 3.

The corrosion rate is more increased with the rise of temperature for uninhibited acid solution. The presence of inhibitor leads to decrease of the corrosion rate. The inhibitory action of inhibitor is slightly reduced at elevated temperature leading to the decreases of E%.
The apparent activation energy is easily determined by the following relations:

$$W_{corr} = k \exp(-E_a / RT) \text{ and } W'_{corr} = k' \exp(-E'_a / RT) \qquad (2)$$

W'_{corr} and W_{corr} are the corrosion rates of steel with and without inhibitor, respectively. E_a' and E_a are the apparent activation energies in the presence and absence of inhibitor, respectively (Take in Table 3).

Table 3 : Effect of temperature (298-318 K) on the corrosion inhibition of steel 1M HCl by epoxy- allylpulegols (**5-7**) at 1 hour.

Compounds 5-7	**T (K)**	**W (mg/cm^{2}h)**	**W_0 (mg/cm^{2}h)**	**E (%)**
Epoxy-allylpulegol **5**	308	0.445	2.121	79
	318	1.135	4.203	73
	328	2.514	7.856	68
	338	5.060	12.65	60
Epoxyallylpulegol **6**	308	0.615	2.121	71
	318	1.555	4.203	63
	328	3.456	7.856	56
	338	6.578	12.65	48
Epoxy-allylpulegol **7**	308	0.678	2.121	68
	318	1.681	4.203	60
	328	3.613	7.856	54
	338	6.831	12.65	46

Straight lines of Arrhenius plots are obtained. The evaluation of activation energies are deduced from the corresponding slopes (Fig. 5). Values obtained are 52.5, 69.1, 68.5 and 66.7 kJ/mol for free acid and in added with **5, 6** and **7**, respectively.

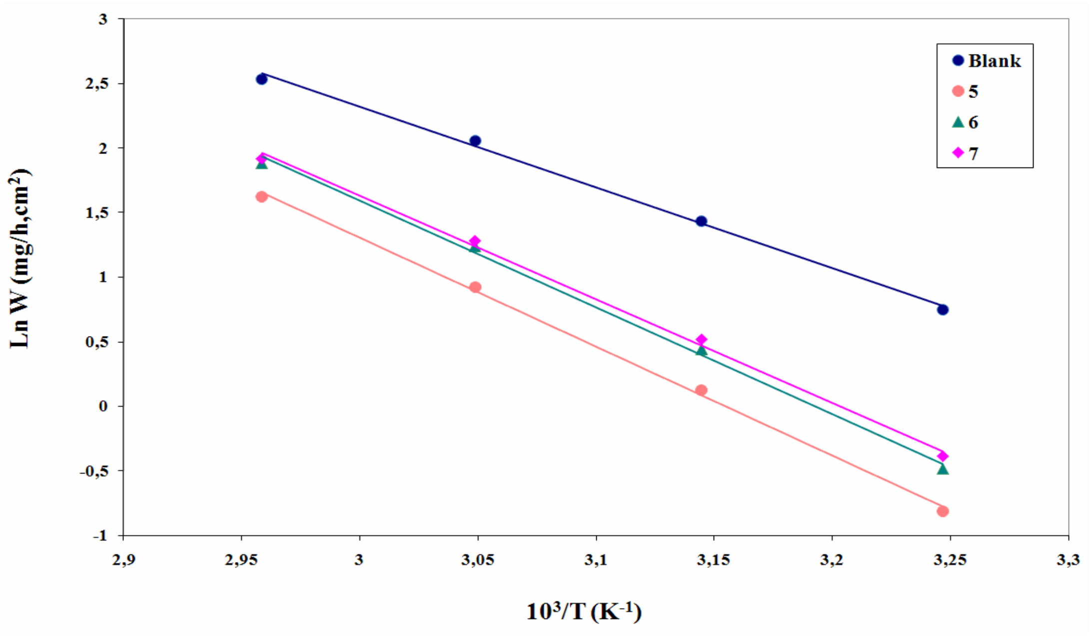


Figure 1: Arrhenius plots of steel in uninhibited and inhibited acid

Increase in the inhibition efficiency with temperature is regarded by Ammar and El Khorafi [30] as the likely specific interaction between the metal surface and the organic compound. The lower value of the activation energy of the process in presence of the inhibitor when compared to that in its absence is attributed to its chemisorption. While the higher Ea is attributed to physical adsorption [31]. Putilova et al. [32] interpreted the chemisorption at higher temperatures by an increase of the surface covered by inhibitor's concentration increase and rate determining step of the metal dissolution becomes the diffusion through the film of corrosion products and inhibitor.

Oguzie [33] explained the decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism [34].

The dependence of the fraction of report C/θ as function of the concentration (C) of epoxy-allylpulegols was graphically fitted. Fig. 2 shows the dependence of of the C/θ as function of the concentration of **5**, **6** and **7**.

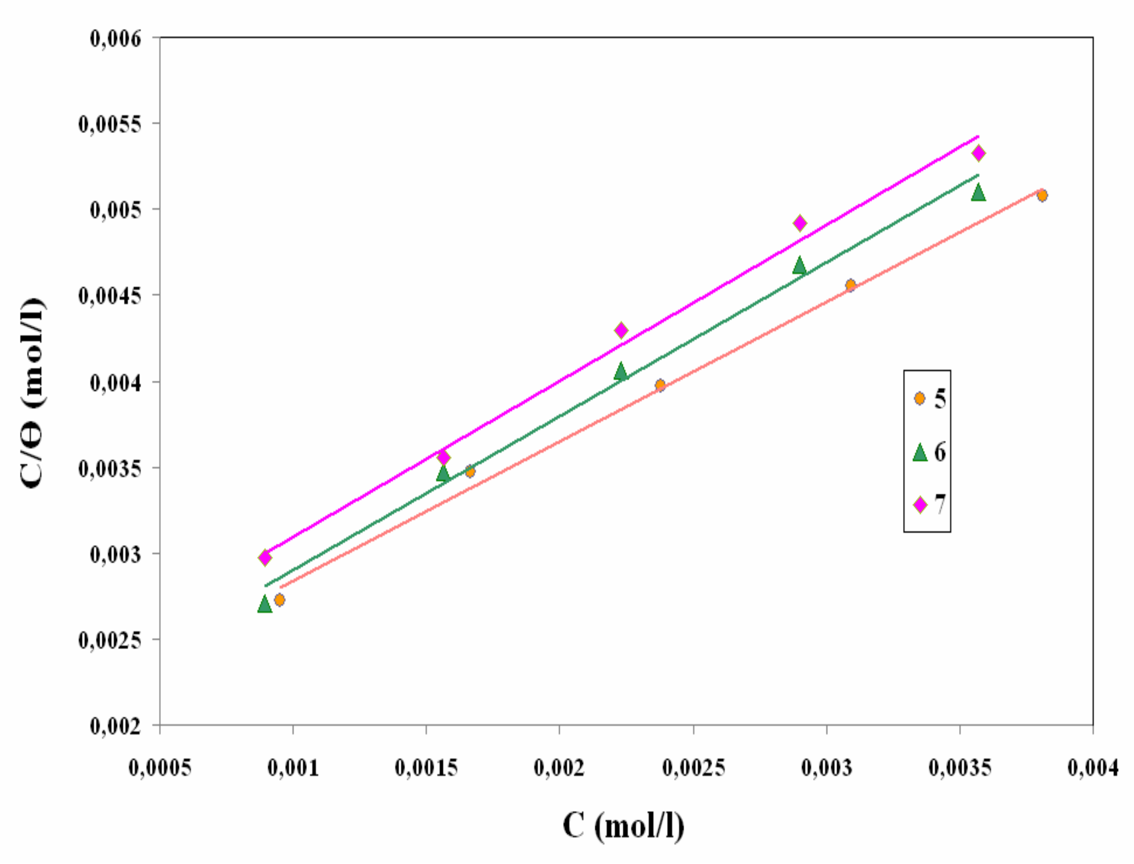


Figure 2: Adsorption isotherm model of epoxy-allylpulegols **5-7**

As can be seen from figure 2 adsorption of exyallylpulegols **5-7** obeys the Longmuir isotherm given by equation

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{b} + C_{\text{inh}} \qquad (3)$$

where b is the equilibrium constant of adsorption adsorption/desorption process, θ **is** Surface covered and C is the inhibitor concentration.

It is admitted that organic compounds having functional groups such as –OR, –C=O, –COOR, –NR2 and/or –SR inhibit corrosion of metals in acidic media [35-37]. The adsorption of organic compounds on metal surface is explained by the substitution of water molecules which facilitate the access of hydrogen ions to the surface and then the corrosion attack. This replacement may cover the metal surface and then reduces the surface area that is available for the attack of the aggressive ion from the acid solution. The corrosion rate decreases with increase with the inhibitor concentration.

As shown in Fig. 2, straight lines are obtained, when C/θ is plotted against C and the linear correlation coefficient of the fitted data is good (>0.995). This result corroborates that the inhibition is due to the adsorption of the inhibitors onto the metal surface and the adsorption obeys the Langmuir isotherm. The calculated values of $\Delta G°_{ads}$ are negative (Table 4). The increasingly negative adsorption free energy ($\Delta G°_{ads}$) reflects the spontaneity of the adsorption of the inhibitor molecules and more $\Delta G°_{ads}$ is negative and more the adsorbed layer on steel surface is stable.

Table 4: adsorption parameters of oxy-allylpulegols on the steel surface in acid solution

Compound	K	ΔG_{ads} (kj/mol)	R^2
5	493.5	-25.3	0.997
6	499.2	-25.3	0.995
7	456.9	-25.1	0.996

The negative values of $\Delta G°_{ads}$ equal -20 kJ/mol or lower are attributed to the electrostatic interaction between the charged molecules and the charged metal (physisorption). Furthermore, those around -40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [38], while values between -20 kJ/mol and -40 kJ/mol indicate both physisorption and chemisorption [39]. The value of -40 kJ/mol is usually adopted as a threshold value between chemi- and physisorption [40]. The values of $\Delta G°_{ads}$ for these Schiff bases point to the spontaneity of the adsorption process under investigated experimental conditions, and it also points out the adsorption of compounds occurs predominantly by physical adsorption [41].

4. Conclusion

From the overall experimental results the following conclusions can be deduced:

1. Allylpulegols **2-4** compounds acts as moderately inhibitors for the corrosion of steel in HCl medium, but their corresponding epoxy-allylpulegols **5-7** give better inhibition;
2. The inhibition efficiency of increases with the epoxy-allylpulegols concentration to attain 79% at 0.8 g/l for **5**;
3. The inhibition efficiency of epoxy-allylpulegols decreases with the rise of temperature.
4. The synthesised molecules adsorb on the steel surface according to the Langmuir isotherm.

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