Evaluation of Anticorrosive Effect of Synthesised Carveol Derivatives on Steel in Hydrochloric Acid

L. Majidi^{1,*}, M. Znini¹, A. Ansari¹, B. Hammouti², C. Jama³, J. Costa⁴, J. Paolini⁴.

¹ Université My Ismail, Laboratoire des Substances Naturelles & Synthèse et Dynamique Moléculaire, Faculté des Sciences et Techniques, Errachidia, Morocco.

² Université Mohamed Premier, LCAE-URAC18, Faculté des Sciences, 60 000 Oujda, Morocco.

³ Unité Matériaux et Transformations (UMET), Ingénierie des Systèmes Polymères, CNRS UMR 8207, ENSCL, BP 90108, F-59652 Villeneuve d'Ascq Cedex, France.

⁴ Université de Corse, CNRS-UMR 6134, Laboratoire de Chimie des Produits Naturels, BP 52, 20250 Corti (France).

^{*}E-mail: <u>lmajidi@yahoo.fr</u>

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Three carveol derivatives (2-phenylcarveol, 2-tolylcarveol and 2-anisylcarveol) were synthesised from carvone to investigate their corrosion inhibition behaviour of steel in 1M HCl using weight loss measurements. The results showed that the addition of these compounds decreases weakly the corrosion rate and increases the inhibition efficiency to reaches 76.6%, 63.14% and 79.6% for **5**, **6** and **7** at 1.2 g/L, respectively. The inhibitor adsorption process in mild steel/**5-7**/hydrochloric acid system was studied at different temperatures (313–323 K) by means of weight loss measurements. The adsorption of compounds **5-7** on steel surface obeyed Langmuir's adsorption isotherm. The corresponding kinetic parameters were determined and discussed.

Keywords: Corrosion Inhibition, Steel, Carvone, Carveol derivatives, Adsorption

1. INTRODUCTION

Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acid media are the major obstacles for its use on larger scale [1]. As acidic media, hydrochloric acid and sulphuric acid are generally used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal [2]. However, the aggressiveness of these acids in the solution against structural materials of mild steel, the use of inhibitors is the most practical methods of protection against corrosion. Their addition is necessary to secure the attack of metal from

corrosiveness media such chemical cleaning and pickling generally used to remove mill scales (oxide scales) from the metallic surface [3]. Though the existing data show that organic compounds have good anticorrosive activity, some of them are highly toxic to both human beings and environment [2,3]. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. Due to increasing environmental awareness and adverse effect of some chemicals, research activities in recent times are geared towards developing cheap, non-toxic and environmentally safe corrosion inhibitors [4].

Previous ours studies [5-8] reported that monoterpenoid compounds (pulegone, epoxypulegone, menthol derivatives, allylpulegols, epoxy-allylpulegols and allyldihydrocarveol) have a wide spectrum of anticorrosive activities. More recently, the allylcarveols, obtained by condensation of allylmagnesium chloride with carvone, have exhibited good inhibitor properties of corrosion of steel in acid media [9]. Furthermore aromatic compounds are known to be very efficient corrosion inhibitior for metal in aggressive media [10]. In the present work, the effect of aromatic substituent on carveol derivatives has been studied on inhibition of corrosion of steel in acid media. For this prupose, three carveol derivatives (2-phenylcarveol, 2-tolylcarveol and 2-anisylcarveol) have been synthesised for the first time from carvone and their inhibitor properties on corrosion of steel in 1 M HCl evaluated using weight loss measurements.

2. MATERIALS AND METHODS

2.1. Synthesis of 2-arylcarveol derivatives (5-7)

The general procedure for the addition of arylic Grignard reagents (2-4) to carvone 1 was carried out as follows (figure 1) : Magnesium (1,1g) was recovered by anhydrous ether (10ml) and was actived by 1,2-dibromoethane. Upon cessation of gas evolution, a solution (2,25 mmol) of arylic bromide (2-4) in 20 ml of anhydrous ether was added dropwise. Carvone 1 (7,5mmol) in 60 ml of anhydrous ether was added dropwise to the reaction flask at 0°C. The reaction mixture was stirred an ice bath for 12 h and then poured onto diluted sulphuric acid solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed to neutrality and dried (Na₂SO₄). The solvent was evaporated and the residual oil was purified by flash chromatography (silica gel/hexane). Infrared (IR) spectra were recorded on Schimatzu IR-470. ¹H NMR spectra were determined on a Brüker AC250 (250 MHz) spectrometer with Me₄Si as the internal standard. ¹³C NMR spectra of CDCl₃ solution were recorded on Brüker AC250 (60 MHz).

2-phenylcarveol 5 ($C_{16}H_{21}O$): IR (film): 3420, 3083, 2990, 1640, 1440, 1020, 980, 902, 886, 705cm⁻¹ ¹H NMR (CDCl₃): 1.60 (3H, s), 1.64 (3H, s), 2.10 (5H, m), 4.60 (2H, m), 5.80 (1H, m), 7.30 (5H, m). ¹³C (CDCl₃): 18.0 (q), 20.8 (q), 31.3(t), 37.9 (s), 45.3 (d), 109.0 (d), 126.4 (d), 126.6 (d), 127.1(d), 128.1 (d), 136.0 (s), 145.8(s), 148.7(s).

2-tolylcarveol 6 (C₁₇**H**₂₇**O):** IR (film): 3460, 3082, 2995, 1648, 1450, 1025, 945, 890, 696cm⁻¹. ¹H NMR (CDCl₃): 1.62 (3H, s), 1,68 (3H, s), 2,12 (3H, s), 2,41 (5H, m), 4,70 (2H, m), 5,90 (1H, m), 7,61 (4H, m). NMR ¹³C (CDCl₃) : 148.6 (s), 142.8 (s), 136.4 (s), 136.2 (s), 128.8 (d), 126.2 (d), 115,1 (t), 109,0 (d), 77.2 (s), 45.5 (d), 38.0 (t), 31.2 (t), 20.7 (q), 20.5 (q), 18,0 (q).

2-anisylcarveol 7 ($C_{17}H_{27}O_2$) : IR (film): 3450, 3082, 2990, 1645, 1035, 985, 880, 920, 725cm⁻¹. ¹H NMR (CDCl₃): 1.60 (3H, s), 1.70 (3H, s), 2.13 (5H, m), 2.19 (3H, s), 4,80 (2H, m), 5.71 (1H, m), 7.20 (4H, m). NMR ¹³C (CDCl₃): 148.9 (s), 140.4 (s), 138.0 (s), 136.4 (s), 128.4 (d), 129.2 (d), 113.7 (t), 109.2 (d), 70.4 (s), 55.2 (q), 45.4 (d), 37.9 (t), 31.3 (t), 20.9 (q), 17.7 (q).

2.3. Weight loss measurements

2.3.1. Preparation of materials

The material used in this study was mild steel ($2 \text{ cm } x \ 2 \text{ cm } x \ 0.05 \text{ cm}$) with a chemical composition (in wt.%) of 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron (Fe). For all the experiments, the mild steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (grades 400, 600 and 1200), then washed thoroughly with double-distilled water, degreased with AR grade ethanol, and finally dried at room temperature before use.

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37% HCl with double-distilled water.

2.3.2. Effect of concentration of inhibitors

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL with and without the addition of different concentrations of inhibitors ranging from 0.3 to 1.2 g/L. The immersion time for the weight loss was 6 h at 301 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each case and the mean value of the weight loss is reported using an analytical balance (precision \pm 0.1 mg). Weight loss allowed us to calculate the mean corrosion rate as expressed in mg.cm⁻² h⁻¹.

The corrosion rate (W) and inhibition efficiency Ew (%) were calculated according to the Eqs. (1) and (2) respectively:

$$W = \frac{\Delta m}{S.t}$$
(1)
$$E_{w} \% = \frac{W_{0} - W_{inh}}{W_{corr}} \times 100$$
(2)

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W₀ and W_{inh} are the values of corrosion weight losses (mg/cm².h) of mild steel in uninhibited and inhibited solutions, respectively, S is the area of the mild steel specimen (cm²) and t is the exposure time (h).

2.3.3. Effect of temperature

The change of the corrosion rate with the temperature was studied in 1M HCl during 1 h of immersion, both in the absence and presence of inhibitors at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (313–323 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [11]:

$$W = A \exp\left(\frac{-Ea}{RT}\right)$$
(3)
$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{a}}{R}\right) \exp\left(-\frac{\Delta H_{a}}{RT}\right)$$
(4)

where Ea is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogrado's number, ΔS° and ΔH°_{a} are the entropy and the enthalpy of activation respectively.

2.4. Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin isotherms. The Langmuir isotherm (C/ θ vs C) assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin adsorption isotherm (θ vs C) assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm (θ vs lgC) represents the effect of multiple layer coverage [12]. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitors in acidic media have been evaluated from the Weight loss measurements.

3. RESULTS AND DISCUSSION

3.1. Synthesis of 2-arylcarveol derivatives (5-7)

The stereoselective synthesis of three carveol derivatives **5-7** (2-aryl-p-mentha-6,8-dien-2-ols) was accomplished for the first time (Figure 1). Condensation of arylmagnesium bromide compounds (phenylmagnesium bromide **2**, tolylmagnesium bromide and anisylmagnesium bromide **4**) on carvone **1** leaded to three 2-aryl-p-mentha-6,8-dien-2-ols (2-phenylcarveol **5**, 2-tolylcarveol **6** and 2-anisylcarveol **7**, respectively) with good yields (70, 85 and 81%, respectively). These compounds exhibited the arylic moiety in the axial position and the hydroxyl group in the equatorial position of the cyclohexene ring (chair conformation).



Figure 1. Synthesis of carveol derivatives (5-7)

The reaction, in all cases, is stereoselective and the alkylation of **1** takes place on the "si face" in a quasi-equatorial fashion. The ¹³C NMR spectrum of each alcohol **5-7** was consistent with the presence of only one diastereoisomer. The structure of alcohols **5-7** was proved by IR and NMR spectroscopy (see experimental section 2.1). Their IR spectra lack carbonyl absorption but contain band at 1645 cm⁻¹ and 3420 cm⁻¹, typical of stretching vibration of C=C bond and associated hydroxyl group, respectively. The ¹H NMR spectra of these compounds showed signals from protons of both p-menthene fragment and massifs due to protons of arylic moieties.

The stereochemistry at the carbinol center of compounds **5**-**7** was initially assigned based on the relative chemical shifts of the carbinol centers in the ¹³C NMR spectra. The signal for the carbinol carbon appears at lower fields for an equatorial than axial hydroxyl group [13]. The carbinol signal further downfield should belong to the axial-addition product. These data are in accordance with previous studies reported by Majidi, et al. [14] and Ito et al. [15]; the authors showed that the addition of allylic magnesium bromide to cycloalkenone is stereoselective and the attack occurs from the axial side of the molecule.

3.2. Gravimetric results

3.2.1. Effect of concentration

The values of corrosion rate (W_{inh}) and the corresponding inhibition efficiency (Ew %) of different concentrations of carveol derivatives 5-7 are given in Table 1 and Fig. 3.

Fig. 3 (a) showed clearly that the corrosion rate (W_{inh}) decreased and the inhibition efficiency increased with increasing concentration of three inhibitors **5-7** at 303 K, i.e. the corrosion inhibition enhances with the inhibitor concentration. Table 1 showed also that the maximum values of the inhibition efficiency (Ew) are 76.6%, 63.14% and 79.6% for **5**, **7** and **8** at 1.2 g/L, respectively, which indicates that carveol derivatives **5-7** acts as a good inhibitors for steel in 1M HCl. This behaviour is due to the fact that the adsorption coverage of inhibitors on metal surface increases with the inhibitor concentrations resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium. This adsorption is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical structure of inhibitors [15]. Indeed the substitution of the allylic moiety by arylic group in carveol derivatives increases the inhibition efficiency [9].

Table 1. Influence of carveol derivatives 5-7	concentration	on the steel	corrosion in	1M HCl at 3	01 K
during 6 hour of immersion.					

Inhibitors	C (g/L)	C (10 ⁻³ mol/L)	W_{inh} (mg/cm ² h)	$E_w \%$
Blank	0	0	9.806	
5	0.3	1.32	6.080	38
	0.5	2.19	5.021	48.8
	0.8	3.50	3.658	62.7
	1	4.39	3.089	68.5
	1.2	5.26	2.295	76.6
6	0	0	9.806	
	0.3	1.24	8.041	18
	0.5	2.07	6.864	30
	0.8	3.31	5.393	45
	1	4.13	4.040	58.8
	1.2	4.96	3.614	63.14
7	0	0	9.806	
	0.3	1.16	5.491	44
	0.5	1.94	4.354	55.6
	0.8	3.10	3.109	68.3
	1	3.86	2.536	74.14
	1.2	4.65	2.000	79.6





Figure 3. Variation of corrosion rate (W_{inh}) (a) and inhibition efficiency (Ew) of corrosion (b) of mild steel in 1 M HCl in the presence of carveol derivatives **5-7** at various concentrations at 301 K.

3.2.2. Effect of temperature and activation parameters Ea, ΔS_a^{o} , ΔH_a°

The effect of temperature on the corrosion inhibition with and without carveol derivatives **5-7** is shown in Table 2 and Fig. 4.

Table 2. Effect of temperature (313-328 K) on the corrosion inhibition of steel 1M HCl by carveol derivatives **5-7** at 1 hour of immersion.

	ТК	W_{inh} (mg/cm ² h)	$W_0 (mg/cm^2h)$	Е %
_	313	0.733	1.980	63
5	318	1.066	3.333	68
	323	1.470	4.900	70
	328	2.029	7.600	73.3
	313	1.162	1.980	41.3
6	318	1.450	3.333	56.5
	323	1.833	4.900	62.6
	328	2.637	7.600	65.3
_	313	0.483	1.980	75.6
7	318	0.633	3.333	81
	323	0.833	4.900	83
	328	1.216	7.600	84



Figure 4. Variation of corrosion rate (W) (a) and inhibition efficiency (Ew) of corrosion (b) of mild steel in 1 M HCl with different temperatures in the absence and presence of compounds **5-7**

It is clear that the corrosion rate (W) is more increased with the rise of temperature for uninhibited acid solution, whereas, the presence of inhibitor leads to decrease of the corrosion rate. In contrast, the inhibitory action of inhibitor is slightly increased at elevated temperature. Hence, we note that the efficiency depends on the temperature and decreases with the rise of temperature from 318 to 328 K. This can be explained by the increase of the strength of the adsorption process and the inhibitory effect of inhibitors is reinforced at elevated temperature.



Figure 5. Arrhenius plots for mild steel corrosion rates (W) in 1M HCl in absence and in presence of 1.2 g/L of carveol derivatives 5-7.



Figure 6. Transition-state plots for mild steel corrosion rates (W) in 1M HCl in absence and in presence of 1.2 g/L of carveol derivatives 5-7.

The apparent activation energy (E_a) was determined from the slopes of Ln (W) vs 1/T graph according to Arrhenius plots depicted in Fig. 5, and the entropy of activation ΔS°_{a} and the enthalpy of activation ΔH°_{a} were determined from the plot of Ln (W/T) vs 1/T graph depicted in Fig. 6. Straight lines are obtained with a slope of ($\Delta H^{\circ}_{a}/R$) and an intercept of (lnR/Nh+ $\Delta S^{\circ}_{a}/R$) from which their values of these kinetic parameters are calculated and are listed in Table 3.

Table 3. Corrosion kinetic parameters for mild steel in 1M HCl in the absence and presence of 1.2 g/L of compounds **5-7**.

Inhibitors	A (mg.cm ⁻² .h ⁻¹)	$E_a(kJmol^{-1})$	ΔH°_{a} (KJ.mol ⁻	Ea–∆H°a	$\Delta S^{\circ}_{a} (J.mol^{-1}.K)$
1M HCl	7.99 10 ¹²	75.59	72.90	2.69	-6.82
5	3.12 10 ⁹	57.73	55.04	2.69	-72.13
6	$5.06\ 10^7$	45.90	43.22	2.68	-106.41
7	2.14 10 ⁸	51.94	49.25	2.69	-94.43

The calculated values of activation energies from the slopes are 75.59 kJmol⁻¹ for free acid and 57.73, 45.90 and 51.94 kJmol⁻¹ with the addition of 1.2 g/L of **5**, **6** and **7**, respectively. It was found that, E_a values for uninhibited system are higher than E_a for inhibited systems. Due to this decrease in the activation energy the dissolution reaction of mild steel decreases in 1M HCl medium. The tendency of variation in pre-exponential factor (A) is similar to that in apparent activation energy. The experimental fact that the activation energy is lower in the presence of inhibitors is explained in different ways in the literature. The increase of inhibition efficiency (E_w), accompanied by the decrease

in activation energy (E_a) with in temperature in the presence of compounds 5-7 can be attributed to an appreciable increase in the adsorption of these inhibitors. This result may be interpreted as chemical adsorption on the mild steel surface [7,8].

Moreover, inspection of the data of Table 3 reveals that the ΔH°_{a} values for dissolution reaction of mild steel in 1M HCl in the presence of 1.2 g/L of three inhibitors are lower than that uninhibited system. The positive signs of ΔH°_{a} reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow in the presence of inhibitors [16]. The average difference value of the $E_a - \Delta H^{\circ}_{a}$ is 2.69 kJ mol⁻¹, is approximately equal to the average value of RT (2.69 kJ mol⁻¹) at the average temperature (323 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known of perfect gas [17].

On the other hand, the entropy of activation (ΔS°_{a}) in the absence and presence of carveol derivatives 5-7 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 [16,17].

3.3. Adsorption isotherm and energy of adsorption, ΔG^{0}_{ads}

The dependence of the fraction of the surface covered θ obtained by the ratio E%/100 as function of the inhibitors concentration (C_{inh}) was graphically fitted for various adsorption isotherms.

Fig. 7 shows that the relationship between C_{inh}/θ and C_{inh} , at 301 K, for 5 and 7, yields a straight line with correlation coefficient (R^2) was almost equal to unity and the slopes were very close to unity. Also, Fig. 8 shows that the plot $Ln(\theta/1-\theta)$ vs. LnC_{inh} was found to be linear for 6, with correlation coefficient (R^2) was almost equal to unity and the slopes were very close to unity.

This behaviour suggests that the adsorption of compounds **5-7** on mild metal surface followed the Langmuir adsorption isotherm suggesting that **5-7** molecules are adsorbed over the metal surface forming a barrier, which prevents the contact of the metal with electrolyte. This isotherm may be written in the following form:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh}$$
(5)
Or
$$Ln\left(\frac{\theta}{1-\theta}\right) = Lnb + LnC_{inh}$$
(6)

where C_{inh} is the inhibitor concentration; θ is the fraction of the surface covered, b is the equilibrium constant of the adsorption process which is related to the standard Gibbs energy of adsorption, ΔG^0_{ads} , according to [15]:

$$b = \frac{1}{55,5} \cdot \exp(-\frac{\Delta G^{\circ}_{ads}}{R.T})$$
(7)

where R is the universal gas constant, T is the thermodynamic temperature, and the value of 55.5 is the concentration of water in the solution in mol/L. The b values and ΔG^0_{ads} were calculated and are presented in Table 4.



Figure 7. Langmuir's isotherm for adsorption of 5 and 7 on steel surface in HCl (Plot of C/ θ vs. C).



Figure 8. Langmuir's isotherm for adsorption of 6 on steel surface in HCl (Plot of $Ln(\theta/1-\theta)$ vs. LnC)

Table 4. The values of equilibrium constant (b) and ΔG_{ads}^0 of carveol derivatives **5-7** on mild metal surface in 1M HCl at 301 K.

Inhibitors	b (L/mol)	$-\Delta G^{0}_{ads}$ (kJmol ⁻¹)
5	404.20	25.09
6	5079.66	31.43
7	604.96	26.10

The standard free energy of adsorption ΔG^0_{ads} , which can characterize the interaction of adsorption molecules and metal surface, was calculated. The large negative values of ΔG^0_{ads} ads ensure

the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [16] as well as a strong interaction between the carveol derivatives **5-7** molecules and the metal surface [17].

Generally, values of ΔG^0_{ads} up to -20 kJ mol⁻¹, the types of adsorption was regarded as physisorption, the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol⁻¹ or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [6]. Here, the calculated ΔG^0_{ads} values are ranging between -25.09 and -31.43 kJ mol⁻¹, indicating that the adsorption mechanism of Arrylcarveols **5-7** on mild steel in 1 M HCl solution at the studied temperatures is both electrostatic-adsorption (ionic) and chemisorption (molecular).

Moreover, the adsorption process depends on the electronic characteristics of the inhibitor, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity [18]. In fact, the solvent H₂O molecules could also be adsorbed at the metal/solution interface. Therefore, the adsorption of inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the inhibitor in the aqueous phase Inh(sol) and water molecules at the electrode surface H₂O(ads) [19]:

 $Inh_{(sol)} + xH_2O_{(ads)} \leftrightarrow Inh_{(ads)} + xH_2O_{(sol)}$ (8)

where x is the size ratio, that is, the number of water molecules re-placed by one organic inhibitor.

3.4. Mechanism of inhibition of carveol derivatives 5-7

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. The organic compounds containing N, S and O are known to be effective inhibitors. Its effectiveness depends on the electron density at the functional groups. The electron density can be varied with the help of suitable constituents and thus the inhibition action of an inhibitor [3].

Therefore, the adsorption of the carveol derivatives **5**-**7** at the metal surface is through the already adsorbed chloride ion. In acidic solutions, the compounds **5**-**7** molecules can exist as cations and adsorb through electrostatic interactions between the positively charged carveol derivatives **5**-**7** cations and adsorbed chloride ions. Owing to the acidity of the medium, the compounds **5**-**7** can exist as a neutral species or in the cationic form. Thus, the adsorption of the neutral **5**-**7** molecules could occur due to the formation of links between the d orbital of iron atoms, involving the displacement of water molecules from the metal surface, and the lone sp² electron pairs present on the oxygen atoms. In addition, the presence of electron releasing character of -OH group may be attributed to the increased electron density leading to electron transfer mechanism from functional group to metal surface [20].

4. CONCLUSION

Three 2-arylcarveol derivatives (2-phenylcarveol, 2-tolylcarveol and 2-anisylcarveol) were synthesised for the first time by addition of arylmagnesium bromide on carvone. These carveol derivatives with aromatic ring exhibited strong inhibitor properties on corrosion of mild steel in HCl medium than allylcarveols. Indeed, the substitution of the allylic moiety by arylic group in carveol derivatives increases the inhibition efficiency.

The inhibition efficiency increased with temperature and with compound concentrations. Finally, the results showed that 2-arylcarveol derivatives were adsorbed on mild steel surface by a spontaneous process and this adsorption fits a Langmuir isotherm model.

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