

Experimental and Theoretical Evaluation of Allicin as Corrosion Inhibitor for Carbon Steel in Sulfuric Acid

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Abstract

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The use of Allicin as green corrosion inhibitor for 1018 carbon steel in 0.5 M sulfuric acid has been evaluated by using potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS) measurements. Tests were carried out under static and dynamic conditions in a concentration range from 0 to 800 ppm. Results show that Allicin is a good mixed type of corrosion inhibitor with its efficiency increasing with an increase in its concentration up to 400 ppm and it decreased with a further increase in its concentration. Inhibitor efficiency decreases with an increase in the testing temperature, but it increases also as time elapsed or by enhancing the mass transport. Theoretical calculations have been performed by using density functional theory (DFT) in order to know the relationship between the electronic properties of Allicin and its inhibitive effect.

1. Introduction

The well-known problems associated with corrosion of metals and alloys is attracting the attention from both academic and industrial points of view in search of a sustainable solution that prevents further economic losses [1]. In industrial processes such as acid pickling, acid cleaning and well oil acidizing, metals and alloys are exposed to corrosive environments such as sulfuric (H_2SO_4), hydrochloric (HCl) and phosphoric acid (H_3PO_4) among others, which causes corrosion and deterioration of them [2]. Among the different methods to prevent corrosion of metals and alloys, the use of corrosion inhibitors is one of the most widely used [3]. Several synthetic chemicals have been used to prevent the corrosion of metals and alloys, and in particular steel, in different environment [4-6]. However, most of these synthetic compounds, which indeed show very good corrosion inhibition properties, are very expensive, highly toxic to the environment and human people, causing severe damage to the environment. Therefore, the use of eco-friendlier inhibitors is needed. In the last few years, the use of extracts from seeds, leaves, roots, etc., naturally occurring corrosion inhibitors has gained increased attention [7-15]. Khan et al. [7] carried out a review of the literature that reports the use of green corrosion inhibitors and found that those compounds which have N, S or O in their molecular structure showed excellent corrosion inhibition properties. Anupama [8] evaluated the use of *Pimentadioica* as corrosion inhibitor for mild steel in HCl by using electrochemical techniques and weight loss measurements. In addition, they used computational calculations for the molecular components to study the corrosion inhibition mechanism. Hussin et al. [9] evaluated the modification of lignin by incorporation of aromatic scavengers, 2-naphthol, AHN EOL and 1,8-dihydroxyanthraquinone, AHD EOL, improving the lignin inhibition properties for mild steel in HCl. Zhang [10] studied the synergistic effect of polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), polyamino polyether methylene phosphonate (PAPEMP), sodium gluconate (Glu) and Zn²⁺ as corrosion inhibitors for carbon steel in soft water, finding that their combination in relatively low dosage provides

excellent corrosion inhibition. Ji et al. [11] used *Musa paradisiac* (Banana) peels as corrosion inhibitor for mild steel in HCl finding a good corrosion inhibition, but raw banana peels extract had a better efficiency tan that for the ripe ones. Ngobiri evaluated *Brassica oleracea* as a green inhibitor for pipeline steel in $0.5M H_2SO_4$ [12]. They found that the corrosion inhibition efficiency increased with the inhibitor concentration and temperature up to a point, but decreased with a further increase in either the concentration or the temperature. Similar studies were performed with mild steel in HCl by using extracts of *Retamamono sperma* [13] and *Eleusineae gyptiaca* and *Croton rottleri leaf* [14].

Garlic is one of the edible plants which has generated a lot of interest throughout human history as a medicinal panacea. Chinese, Greeks, Egyptians use garlic since memorial times to treat heart disease, arthritis, abdominal growths, etc... Nowadays, use of garlic is rising in the health conscious population. Reports suggest that it has beneficial effects in diseases such as ischemic-reperfusion arrhythmias and infarction [15], ischemic heart disease, hypertension, hyperlipidaemia [16], peripheral arterial occlusive disease and hypercholesteraemic atherosclerosis [17]. The above beneficial effects of garlic in the stated diseases and other undocumented health problems may be due to its antioxidant properties. These antioxidants are also effective against ischemia-reperfusion cardiac injury and hypercholesterolemia atherosclerosis [18, 19]. Allicin is the major component of garlic which has antibacterial, antiviral and antiparasitic effects [20, 21]. It has been claimed that Allicin can help to prevent cancer risk [22, 23]. Allicin, with a chemical structure as given in Fig. 1, also reduces serum cholesterol and triglyceride levels as well as atherosclerotic plaque formation, prevents platelet aggregation and decreases blood pressure [24-25]. Thus, the goal of this paper, is to evaluate the inhibitory properties of Allicin for carbon steel in sulfuric acid, one of the most used reagents in the chemical industry.



Figure 1. Chemical structure of Allicin

2.Experimental procedure

2.1*Testing* material

Testing material includes 1018 carbon steel rods with a diameter of 6.00 mm and 20.00 mm long, which were encapsulated in commercial epoxy resin. Specimens were ground with 600 grade emery paper, rinsed with water and dried with warm air.

2.2Allicin obtention

A liquid to liquid extraction with dichloromethane was made at the methanol extract of garlic to recover the less polar fraction, which could contain Allicin. The followed method of extraction was modified from Bakht [26]. The garlic bulbs slides (930 g) were put into an Erlenmeyer flask and 2.0 L of methanol were added and left during 72 h. After this time, the dissolvent was eliminated by reduced pressure distillation with a Buchi rotary evaporator until the volume was reduced down to 200 mL. Distilled water (200 mL) was added to the dichloromethane phase andthen combined with the methanol extract and the methanol-water mixture was extracted with dichloromethane; this was repeated three times. The extractions were reunited and the excess of dissolvent was eliminated with the Buchi rotary evaporator. The residue was considered a less polar fraction coming from the garlic methanol extract and used as green inhibitor.

2.3 Infrared Spectroscopic analysis

The less polar fraction coming from garlic methanol extract used as corrosion inhibitor was examined under FTIR analysis by using Bruker equipment with a wave lamp in the 4500-400 cm⁻¹ interval and the sample was prepared as KBr pellet. The peak values of the FTIR were recorded. Each analysis was repeated twice to detect the characteristic peaks and their functional groups.

2.4 Gas Chromatography / Mass spectrometry (GC-MS) analysis

The less polar fraction coming from the garlic methanol extract employed as green corrosion inhibitor was also analyzed on a GC Agilent 6890 System Plus coupled to Agilent 5973 Network Mass selective detector, to detect the main organic natural compounds contained in the extract. The GC-MS was equipped with silica capillary column (30 m X 0.25 mm, film thickness 0.25 mm). The GC working temperaturewas at the interval 45 to 250 $^{\circ}$ C with a temperature gradient of 10 $^{\circ}$ C/min. A volume 1.0 μ L of extraction with a concentration of 0.02 g/L

was injected. The identification of the majority of components was based on the comparison of their mass fragmentation indexes with those of authentic compounds on the commercial equipment high quality mass spectra database N-15598.

2.5 *Electrochemical techniques*

Employed electrochemical techniques includes potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements. A standard three electrode glass cell was used for these experiments, with a Silver/Silver chloride electrode (SCE) as reference electrode and a graphite rode as auxiliary electrode. Before starting the experiments, the free corrosion potential value, E_{corr} , was measured until it reached a stable value, normally 30 minutes. For potentiodynamic polarization curves, steel was polarized from -1000 up to +2500 mV with respect the E_{corr} value, at a scan rate of 1 mV/s. Inhibitor efficiency percent values. I.E. were obtained according to the next equation:

$$I.E.(\%) = 100(Icorr_1 - Icorr_2)/Icorr_1$$
 (1)

where I_{corr1} is the current density value without inhibitor and I_{corr2} is the current density value with inhibitor, which were calculated by using the Tafel extrapolation method. EIS measurements were carried out at the E_{corr} over the frequency range value 10 KHz-0.5 Hz with a perturbation 10 mV in amplitude. Inhibitor efficiency values were calculated by using

I.E. (%) = 100 (
$$R_{ct1} - R_{ct2}$$
)/ R_{ct1} (2)

where R_{ct1} is the charge transfer resistance with inhibitor and R_{ct2} the charge transfer resistance without inhibitor. Experiments were carried out at roomtemperature (25 °C), 40 and 60 °C for triplicate. In order to assess the mass transport effect, some tests were carried out at different speed rotations by using a rotating disc electrode. Cylindrical specimens 10 mm long with a diameter of 6 mm were machined and embedded in PTFE exposing an effective surface area of 1.13 cm² to the electrolyte. This system was machined to form the rotating disk electrode, which was ground up to 600 grade emery paper, rinsed with distilled water, acetone, and dried under an air flow. Rotating speeds included 250, 500, 1000 and 2000 rpm.

2.6 Computational studies

For the geometry optimization, frontier molecular orbitals and local chemical reactivity calculations, the electronic structure method of density functional theory (DFT) with the hybrid functional B3LYP was applied [27, 28] in combination with the 6-311G(d,p) People type basis set. Ground state structure of the Allicin molecule was fully optimized with the above mentioned method and the optimized structural parameters were used for the analytical frequency calculations, where the absence of imaginary frequencies confirmed that the stationary points correspond to the global minima of the potential energy hypersurface. It is well known that the phenomena of electrochemical corrosion appear in liquid phase, and for this reason it is necessary to include in the computational calculations the effect of a solvent. All the theoretical calculations were determined in gas phase through the approximation of an isolated molecule, while the solvent effects were considered by the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) in water as a solvent.

3.Results and discussion

3.1 Infrared Spectroscopic Analysis

The FTIR spectrum for the less polar fraction coming from the garlic methanol extract is shown in Fig.2. The signals exhibit at 3418 cm⁻¹ a typical signal for a O-H bond, whereas at 1220 cm⁻¹ appears the signal for the C-O bond. The signals at 2924, 1432 and 753 cm⁻¹ distinguish the C-H for (sp³ carbons) and -CH₂-bonds. The signals at 1642, 1515 and 928 cm⁻¹ distinguish the double C=C, C-H bonds and the neighbor =C-Hdouble bond respectively. The signals at 1125 and 1039 cm⁻¹ show the vibrations for the S=O bonds, whereas the signals at 657 and 506 cm⁻¹ exhibit the –S-S- and C-S bonds. It is clear the presence of acyclic thiosulfinates compounds (Fig.1) which are characteristics for garlic [20, 21, 31, 32].

3.2 Gas Chromatography / Mass spectrometry (GC-MS)

In garlic, Allicin (diallylthiosulfinate) is the responsible compound for the antimicrobial activity [20, 21, 29, 30]. However, it is very thermo-labile and produces various disulfide compounds on heating [31]. The analysis of this methanol garlic extract was carried out at a highertemperature (280 °C) after injection into the equipment.



Figure 2. Infrared spectrum of the garlic methanol extract

High temperature always leads to thiosulfinate compounds decomposition [32]. The presence of Allicin is only confirmed in fresh garlic extracts because it could be decomposed in the injection port of GC ant to produce vinyldithiins [33] and its presence was not confirm by this technique. Six compounds were separated and identified by GC-MS in the garlic methanol extract. The chemical identification is given on table 1 whereas the structures of the compounds found are given in Fig.3.



Figure 3. Identified compounds in the garlic methanol extract through GC-MS. Names are given in table 1

MS.				
$t_{\rm r}$ (min)	RA (%)	[M]+	Compound name	Fragmentation
18.99	7.55	270	Hexadecanoic acid, methyl ester	239, 227, 213, 199, 185, 171, 157, 143,
				129, 97, 87, 74, 55, 43
19.38	13.90	256	n-Hexadecanoic acid	227, 213, 199, 185, 171, 157, 142, 129,
				115, 97, 73, 60, 43
19.66	8.78	284	Hexadecanoic acid, ethyl ester	255, 241, 227, 213, 199, 185, 171, 157,
				143, 129, 115, 101, 88, 73, 55, 43
20.67	40.52	294	9, 12-Octadecadienoic acid (Z,Z)-	263, 234, 220, 205, 192, 178, 164, 150,
			, methylester	136, 123, 109, 95, 81, 67, 55, 41, 29
20.72	5.78	292	9, 12, 15-Octadecatrienoic acid	277, 261, 236, 217, 191, 149, 135, 121,
			(Z,Z,Z)-, methylester	108, 95, 79, 67, 55
21.30	11.31	280	9, 12-Octadecadienoic acid	264, 246, 220, 209, 196, 182, 164, 150,
				136, 109, 95, 81, 67, 55, 41, 29
	DA 1.4	1 1		

Table 1.	Chemical	compounds	identified i	in the less	s polar f	fraction	of the	garlic	methanol	extract by	y using	GC
MO												

 t_r = retention time; RA = relative abundance ; [M]+ = Ion molecular mass

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Results show that according to relative abundance, the main compound was 9, 12-Octadecadienoic acid (Z,Z)-, methyl ester (40.52 %). It is a good antioxidant compound [34]. *n*-Hexadecanoicand 9, 12-Octadecadienoic acids were the second most abundant compound with 13.90 and 11.31 % of relative abundance respectively; on the other hand, the least abundant compounds, with less than 10% of abundance were 9, 12-Octadecadienoic acid, Hexadecanoic acid, methyl ester, Hexadecanoic acid, ethyl ester and 9, 12, 15-Octadecatrienoic acid methyl ester.

3.3 Electrochemical characterization

Polarization curves for 1018 carbon steel in 0.5 M, at 25 0 C at different Allicin concentrationsare shown in Fig. 4, where it can be seen that in all cases, with or without Allicin, data displays an active-passive behaviour. The E_{corr} value was marginally affected by the addition of the inhibitor, but the I_{corr} was decreased, reaching the lowest value with the addition of 400 ppm of Allicin, and it increased with a further increase in the inhibitor concentration. For the blank, uninhibited solution, the passive zone started at 795 mV, with a passive current density value, I_{pas} , close to 700 mA/cm² and a pitting potential of 795 mV. However, when Allicin was added, a first unstable passive zone is shown between the E_{corr} value and -445 mV approximately, followed by an increase in the anodic current density value, due to the dissolution of this passive layer. However, a second, more stable passive zone was found at higher potential values, close to 500 mV, where the I_{pas} value decreased more than two orders of magnitude, reaching its lowest value, 1 mA/cm² when 400 ppm of Allicin were added, increasing with a further increase in the inhibitor concentration. The pitting potential value, E_{pit} , increased with the addition of the inhibitor also, from 795 mV, obtained for the uninhibited solution, up to 1600 mV obtained when 600 ppm of Allicin were added, as shown in table 2.



Figure 4: Effect of Allicin concentration in the polarization curves for 1018 carbon steel in 0.5M H_2SO_4 at 25 $^{\circ}C$

Table 2. Electrochemical parameters obtained from the polarization curves for 1018 carbon steel in 0.5 M H₂SO₄ with different concentrations of Allicin.

C _{inh}	E _{corr}	I _{corr}	β_{a}	β _c	I.E.	E _{pit}	Θ	I _{pas}
(ppm)	(mV _{SCE})	(mA/cm^2)	(mV/dec)	(mV/dec)	(%)	(mV _{SCE})		(mA/cm^2)
0	-405	0.5	32	150		795		700
200	-445	0.23	114	160	54	1370	0.54	7
400	-470	0.19	148	180	61	1350	0.61	1
600	-435	0.40	120	145	19	1600	0.19	9
800	-460	0.25	125	170	21	1340	0.21	3

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Thus, if it is clear that the addition of 400 ppm of Allicin decreases the I_{corr} value from 0.5 to 0.19 mA/cm², less than one order of magnitude,but it was more evident the Allicin effect on the I_{pas} value, decreasing its value from 700 down to 1 mA/cm², a decrease in more than two orders of magnitude, making evident the improvement in the passive film properties. From table 2 it is clear that the highest inhibitor efficiency, 61 %, was reached with the addition of 400 ppm, and it decreased with a further increase in the Allicin concentration. The metal surface covered by the inhibitor, Θ , given by dividing the inhibitor efficiency by 100, increased with increasing the inhibitor concentration, reaching its highest value at 400 ppm. Both anodic and cathodic Tafel slopes were modified with the addition of Allicin, although this effect more clear in the anodic branch and it was maximum at 400 ppm, indicating that Allicin acts as a mixed type of inhibitor.

The effect of Allicin concentration in the EIS data in both Nyquist and Bode formats are given in Fig. 5. Nyquist diagrams, Fig. 5 a, show a single depressed, capacitive like semicircle with its centre at the real axis, indicating a charge transfer controlled process. The shape of the semicircle did not change with the addition of Allicin, indicating that the corrosion mechanism remained the same, but the semicircle diameter increased with the inhibitor concentration, reaching the maximum value with the addition of 400 ppm, decreasing with a further increase in the inhibitor concentration. This increase in the semicircle diameter is due to the Allicin adsorption as given in table 2, where it was found that the metal surface covered by the inhibitor, Θ , increased with increasing the Allicinconcentration and it reached its highest value at 400 ppm of Allicin. Some elongations can be seen at the lowest frequency values, which can be due to the accumulation of all kind of species at the metal/solution interface [35, 36] and increase the total impedance value. On the other hand, Bode plots, Fig. 5 b, show a single peak around 200 Hz, indicating the presence of only one phase constant. As the Allicin concentration increases, the phase angle remains constant on a wide frequency interval, and with the addition of 400 ppm, the frequency interval over which the angle phase remains constant was the widest, indicating the presence of a protective film on the steel surface, with two phase constants. Thus, EIS data could be represented by circuit shown in Fig. 6. In this figure, the semicircle diameter corresponds to the polarization resistance, R_p, R_s is the solution resistance, R_{ct} the charge transfer resistance, C_{dl} the double layer capacitance, R_f , is the resistance of all the accumulated corrosion products such as the inhibitor formed filmat the metal/solution interface and C_f its capacitance. The impedance of the constant phase element (CPE) is given by:



Figure 5: Effect of Allicin concentration in the a) Nyquist and b) Bode plots for 1018 carbon steel In 0.5 M H_2SO_4 at 25 ^{0}C



Figure 6: Electric circuit used to simulate EIS data for 1018 carbon steel In $0.5 \text{ M H}_2\text{SO}_4$ at 25 $^{\circ}\text{C}$ in presence of Allicin.

Table 3. Parameters used to simulate EIS data for 1018 carbon steel in $0.5 \text{ M H}_2\text{SO}_4$ with different concentrations of Allicin.

C_{inh}	R _{ct}	C _{dl}	n _{dl}	$R_{\rm f}$	C_{f}	n_{f}	I.E.
(ppm)	$(Ohm cm^2)$	$(\mu F cm^2)$		$(Ohm cm^2)$	$(\mu F cm^2)$		(%)
0	33	153	0.5				
200	103	36.7	0.7	41	300	0.8	66
400	202	31.4	0.9	75	100	0.9	83
600	136	93.7	0.76	53	195	0.86	74
800	141	108.2	0.8	75	70	0.86	75

$$Z_{\rm CPE} = 1/[Y_0(iw)^n]$$
(3)

where Y_0 is the magnitude of the CPE, we the angular frequency and n a physical parameter which gives interphase properties of the working electrode. The R_{ct} values are inversely proportional to the corrosion rate. The double layer capacitance can be calculated by using following equation:

 $C_{dl} = (2\pi f_{max} R_{cl})^{-1}$ (4) where f_{max} is the frequency value where the maximum value of imaginary impedance is found. Results given in table3 indicate an increase in the charge transfer resistance with the Allicin concentration and thus, a decrease in the corrosion rate. The resistance of the film also increases with the Allicin concentration, reaching its highest value at 400 ppm and it decreases with a further increase in the inhibitor concentration. However, it is clear that the charge transfer resistance values are higher than those for the film formed by the inhibitor, indicating that the corrosion resistance is given by the former.On the other hand, the double layer capacitance value, C_{dl} , decreases as the Allicinconcentration increases, reaching its lowest value at a concentration of 400 ppm. A similar behavior was obtained for the capacitance of the film formed by the inhibitor. In addition, the values of the double-layer capacitance (C_{dl}) decrease by adding inhibitor in to corrosive solution. An alternative to calculate the double-layer capacitance value is by using equation:

$$C_{dl} = \epsilon \epsilon_0 A / \delta$$

(5)

where ε is the double layer dielectric constant, ε_0 the vacuum electrical permittivity, δ the double layer thickness, and A the surface area. Thus, the decrease in the C_{dl} value is attributed to the replacement of the adsorbed water molecules at the surface metal by the inhibitor having lower dielectric constant [37]. Also, the decrease in surface area which acts as a site for charging may be considered as another reason for the C_{dl} decrease [38]. These points suggest that the role of inhibitor molecules is preceded by its adsorption at the metal–solution interface. The n_{dl} value was 0.5 for the uninhibited solution and it increases with the Allicin concentration, reaching its highest value of 0.9 with 400 ppm of Allicin.

According to Eq. (3), it is clear that for $n_{dl} = 0$, electrical circuit will show the characteristics of a pure resistor, and $n_{dl} = 1$, electrical circuit will correspond to a pure capacitor. That means that increase in n_{dl} values showed a capacitive behaviour of mild steel in acidic solution in presence of the extracts [39, 40]. However, ideal capacitor behaviour was not observed (n < 1), which might be resulted from irregular surface of electrode due to corrosion. When the steel is exposed to the aggressive solution, it will show some degree of roughness, and the n value is close to 0.5, but when Allicin is added, the corrosion attack on the steel surface is less pronounced, decreasing this roughness, increasing the n value reaching values close to 1.

To assess the retarding behaviour of corrosion inhibitor on a time scale, EIS measurements were carried out in $0.5 \text{ M H}_2\text{SO}_4$ solution in the absence and in presence of Allicin at 400 ppm for different immersion times at 25 $^{\circ}\text{C}$. Results are shown in Fig. 7. It must be noted that in the uninhibited solution, Fig. 7 a, the semicircle diameter value increases only during one or two hours of exposure to the corrosive solution, and, after that time, it started to decrease rapidly, indicating the desorption of any formed film from the steel surface. For the solution containing 400 ppm of Allicin, Fig. 7 b, the semicircle diameter increase during 24 hours, and after that the semicircles diameter starts to decrease, indicating a desorption of the film-formed by the inhibitor. However, even after 60 hours of exposure to the corrosive solution, the semicircle diameter of the solution containing 400 ppm of Allicinis much higher than that obtained for the uninhibited solution, indicating that the film formed by Allicin remains on the surface steel.



Figure 7:Evolution in time of Nyquist diagrams for 1018 carbon steel in 0.5 M H_2SO_4 solution, 25 ^{0}C , containing a) 0 and b) 400 ppm of Allicin

3.4 Effect of temperature

Polarization curves for uninhibited and solution containing 400 ppm of Allicin at different testing temperatures are shown in Figs. 8 and 9 respectively. For the uninhibited solution, Fig. 8, the E_{corr} value was marginally affected, although there was a shift towards more active values whereas the I_{corr} value increased as the temperature increased from 25 to 60 $^{\circ}$ C. Additionally, both anodic and cathodic current density values were increased by the temperature, indicating that the anodic dissolution reaction as well as the hydrogen evolution and oxygen reduction reaction are activated by the temperature. The passive zone was still kept up to 40 $^{\circ}$ C, but it disappeared at 60 $^{\circ}$ C. This effect was more marked for the Allicin containing solution, Fig. 9, where it can be seen that the E_{corr} value shifted towards nobler values and the corrosion current density value increased as the temperature increased. The passive behaviour was shown only at 25 and 40 $^{\circ}$ C but not at 60 $^{\circ}$ C, indicating the degradation of the protective corrosion products formed on the steel surface. This may be due the fact, as it was mentioned above, Allicin contains thiosulfinate compounds which are degraded with increasing the testing temperature [32]. The apparent activation energy, E_a , associated with 1018 carbon steel in uninhibited and inhibited acid solution was determined by using an Arrhenius-type plot according to the following equation:

$$\log I_{corr} = -E_a/2.303RT + \log F$$

where R is the molar gas constant, T is the absolute temperature and F is the frequency factor. An Arrhenius type of plot for log I_{corr} versus 1000/T for uninhibited and solution containing 400 ppm of Allicin is shown in Fig. 10.The apparent activation energy obtained for the corrosion process in the uninhibited acid solution was found to be 12.46 and 20.1 kJ mol⁻¹ in presence of the inhibitor respectively. It is clear that the energy barrier of the corrosion reaction increased in presence of the inhibitor, and therefore the corrosion rate decreases, which can be due to the physisorption of the inhibitor on the steel surface.



Figure 8:Effect of temperature in the polarization curves for 1018 carbon steel in uninhibited 0.5 M H_2SO_4 solution



Figure 9: Effect of temperature in the polarization curves for 1018 carbon steel in 0.5 M H₂SO₄ solution containing 400 ppm of Allicin

The effect of temperature on Nyquist diagrams for 1018 carbon steel in 0.5 M H_2SO_4 solution containing 400 ppm of Allicin is shown in Fig. 11. It can be seen that at 40 ^{0}C data describe a single, depressed , capacitive-like semicircle at all the frequency values, indicating a charge transfer controlled corrosion process, whereas at 60 ^{0}C data describe one capacitive semicircle at high and intermediate frequency values, followed by what looks like an unfinished capacitive semicircle at low frequency values. The first high frequency semicircle is related with the presence of a corrosion products film, whereas the second low frequency values correspond to the double electrochemical layer. The real impedance values decreased with an increase in the testing temperature, indicating thenon-protective nature of the corrosion products due to the degradation of the inhibitor with an increase in the temperature, and thus, an increase in the corrosion rate.



Figure 10: Arrhenius type of plot for log I_{corr} vs. 1000/K for 1018 carbon steel in 0.5 M H₂SO₄ solution, 25 ^oC, containing 0 and 400 ppm of Allicin



Figure 11: Effect of temperature on Nyquist diagrams for 1018 carbon steel in 0.5 M H₂SO₄ solution containing 400 ppm of Allicin

3.5 Mass transport effect

In order to see the effect of the mass transport in the Allicin performance, some electrochemical tests were performed at different speed rotations by using a rotating disc electrode. The effect of rotating speed on the polarization curves for 1018 carbon steel in 0.5 M H_2SO_4 solution containing 400 ppm of Allicin is given in Fig. 12. A dramatic decrease in both anodic and cathodic current density values with an increase in the rotating speed. Flow can increase mass transport of inhibitor molecules that causes more inhibitor presence at metal surface. This effect can improve the inhibitor performance. The inhibitor may then combine with freshly generated Fe²⁺ ions on steel surface, forming metal inhibitor, [Fe-Inh]²⁺, complexes Hydrodynamic conditions can increase mass transport of metal ions (Fe²⁺) produced during metal dissolution from the electrode surface to the bulk solution and hence lead to less [Fe-Inh]²⁺ complex presence on the electrode; this is a harmful effect for inhibition performance. The high shear stress resulted from high flow velocity can also separate the layer of adsorbed [Fe-Inh]²⁺ complex and cause more desorption from the metal surface, which acts as a negative factor on the inhibitor efficiency. The balance of the above mentioned effects lead to changes on inhibitor efficiency with rotation rate, which was benefitial in our case.

The E_{corr} value is shifted towards nobler values and the I_{corr} value decreased with an increase in the rotating speed from 0.5 down to 3 x 10⁻³ mA/cm² at 0 and at a rotating speed of 2000 rpm respectively, as shown in table 4. The passive zone displayed under static conditions is any longer displayed under dynamic conditions. On the other hand, Nyquist diagrams for 1018 carbon steel in 0.5 M H_2SO_4 solution containing 400 ppm of Allicinat different rotating speeds are shown in Fig. 13, where it can be seen that data describe a single, depressed, capacitive like semicircle at all frequency values with its center at the real axis. Semicircle diameter increases with an increase in the rotating speed, from a value of 202 ohm cm² at 0 rpm, up to a maximum value of 1300 ohm cm² reached at a rotating speed of 2000 rpm. Electrochemical parameters obtained for Nyquist diagrams by using electrical circuit shown in Fig. 6 are given in table 5, where it can be seen that both charge transfer resistance and double layer capacitance, (Rct and Cdl respectively) remained unchanged with the different rotating speeds. However, the film resistance value increased, whereas the film and capacitance decreased, which indicates an increase in this film thickness. Additionally, the R_f values were higher than those for R_{ct} , which indicates that the corrosion resistance under dynamic conditions is given by the corrosion products film thickness. The n_{dl} values close to 1 is an indicative that the double electrochemical layer is behaving almost as an ideal capacitor and that the surface is almost homogeneous due to the fact that corrosion attack on the steel surface is marginal.



Figure 12: Effect of rotating speed in the polarization curves for 1018 carbon steel in $0.5 \text{ M H}_2\text{SO}_4$ solution containing 400 ppm of Allicin

Potentiodynamic results show an evident effect on the corrosion behaviour from passivity to activation control as hydrodynamic condition changes, Fig. 12, which was confirmed by the impedance module from EIS shows too Fig. 13. Under static conditions, reactants such as oxygen and inhibitor moves so slowly towards the metal/electrolyte interface that are accumulated at this interface, even when they form a passive film which protects the metal, and this is evident by the elongation shown at low frequency values in the Nyquist diagram under static conditions in Fig. 13. As rotating speed increases, the supply of reactants such as oxygen and inhibitor towards the metal/electrolyte so fast that they react with released Fe^{2+} ions to form the protective film and are not accumulated at this interface, changing the corrosion mechanism from passivity to activation control.

As shown in table 1 and Fig. 3, all the compounds contained in Allicin include in their structures polar heat and nonpolar ends, and in the polar heat have oxygen. It is know that in the corrosion inhibition processes heteroatoms play an important role, because usually they are adsorbed on the electrovalent metal surface and the pair alone electrons the π -orbitals to form a complex with the Fe²⁺ ions through metal interaction [41-43]. Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur, oxygen, or phosphorus. It has been reported that efficiency of inhibition decreases in the order: O > N > S > P [44]. This may explain why the inhibition efficiency of Allicin, whose main component is sulphur, is low, 61 and 83% according to polarization curves and EIS measurements respectively. Adsorption of the positively charged molecule inhibitor would be limited by the concentration of the anions on the metal surface.



Figure 13: Effect of rotating speed in the Nyquist diagrams for 1018 carbon steel in $0.5 \text{ M H}_2\text{SO}_4$ solution containing 400 ppm of Allicin

Table 4. Electrochemical parameters obtained from the polarization curves for1018 carbon steel in 0.5 MH2SO4 at different rotating speeds containing 400 ppm of Allicin.

Rotationspeed(rpm)	E _{corr}	I _{corr}	βa	βc
	(mV _{SCE})	(mA/cm^2)	(mV/dec)	(mV/dec)
0	-405	0.5	32	150
250	-315	4 x 10 ⁻³	170	225
500	-255	1 x 10 ⁻³	115	160
1000	-315	7 x 10 ⁻⁴	105	130
2000	-200	3 x 10 ⁻⁴	95	95

Table 5. Parameters used to simulate EIS data for 1018 carbon steel in $0.5 \text{ M H}_2\text{SO}_4$ at different rotating speeds containing 400 ppm of Allicin.

Speed rotation	R _{ct}	C _{dl}	n _{dl}	$R_{ m f}$	C_{f}	n _f
(rpm)	$(Ohm cm^2)$	$(\mu F cm^2)$		$(Ohm cm^2)$	$(\mu F cm^2)$	
0	202	31.4	0.9	75	10	0.9
250	199	46	0.8	597	91	0.9
500	205	30	0.8	1035	52	0.9
1000	207	25	0.8	1121	24	0.8
2000	198	56	0.8	1203	40	0.9

Allicin molecules may also be adsorbed via donor-acceptor interactions between the metal and unshared electron pairs of the heteroatoms (S, N, O), forming bonds with the vacant d-orbitals of the iron atom on the metal surface, which acts as a Lewis acid, leading to the formation of a protective chemisorbed film [44] as will be explained later.

It is generally accepted that the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules absorbed on the metal surface:

$$Inh_{sol} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O_{sol}(7)$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on steel surface, forming metal inhibitor complexes [45]:

$$Fe \rightarrow Fe^{2+} + 2e$$

$$Fe^{2+} + Inh_{ads} \rightarrow [Fe-Inh]_{ads}^{2+}$$
(8)
(8)

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution. At low concentrations the amount of Allicin is not enough to form a compact complex with the metal ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher inhibitor concentrations, more Allicin molecules become available for the complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion, because under flow conditions there are different effects on the inhibition performance. With an increase in the rotating speed, more inhibitor molecules can arrive to the metal surface, improving the inhibitor performance [46]. At the same time, more Fe⁺ ions can be transported to the bulk solution, leaving a lower amount of these ions available at the metal surface to form the [Fe-Inh]²⁺ complex. And, finally, as a result of the high velocity, the [Fe-Inh]²⁺ complex can be desorbed from the metal surface, leaving unprotected the metal surface [46]. The net result can be harmful or beneficial. In this case, it is clear that with increasing the rotating speed, mass transport of the inhibitor is enhanced and more inhibitor molecules are present at the steel surface to form the protective [Fe-Inh]²⁺ complex.

3.6 Theoretical results

It has been reported that the effectiveness of an inhibitor can be related with its geometrical structure and quantum-chemical parameters, especially those associated with the interactions metal-inhibitor, and these parameters cloud be: the HOMO energy (highest occupied molecular orbital) that is often associated with the capacity of a molecule to donate electrons, the LUMO energy (lowest unoccupied molecular orbital), the gap energy ΔE (the lower values of gap, the better the corrosion inhibition), and the dipole moment, because low values will favor the accumulation of inhibitor molecules on the metallic surface [47]. Fig. 14 shows the optimized geometry structure in a gas and water phases. It can be seen that in the gas phase, a weak interaction between the 4C – 6H \cdots 2O bonds with a value of 2.1320 Å, whereas in the aqueous phase there are two weak interactions with two different hydrogen atoms, 6H and 5H, with a value of 3.4065 Å y 4.3352 Å, respectively.



Figure 14: Optimized structure of Allicin in a) gas and b) aqueous phase. Distances between oxygen and hydrogen neighbour atoms are indicated.

Calculated selected interatomic distances, angles and dihedral angles after the optimization calculations and their comparison with reported data in literature are listed in table 6. As can be inferred from table 6, the obtained values for the studied molecule are very similar to those reported data using different theoretical methodologies. However, the obtained values in the aqueous phase showed a major variation in the 12C - 1S - 3S - 4C dihedral angle with 155.66° , being the average of 87.60° as obtained with different methods.

3.6.1 Frontier molecular orbitals.

The calculations of the frontier molecular i.e. HOMO and LUMO respectively, were done in both gas and solvent (aqueous) phase. It has been reported that the HOMO location in a molecule indicates the preferred sites for the electrophilic attack through metallic cations. As can be seen in Figs. 15and16, the most important zones for the electrophilic attack are located on the oxygen (2O) and sulfur (1S y 3S) atoms present in the structure. 3S atom displays the highest concentration of the HOMO orbital calculated in the gas phase, while in solvent phase the HOMO orbital is almost equally distributed over the mentioned atoms. It is very likely that the parts of the molecule with high HOMO density were oriented towards the metallic surface and the adsorption of these ones could be sharing the lone pair electrons of the oxygen and sulfur atoms, while the short chains of the molecules perform a slight impediment toward corrosive species in the solution.

	1	піѕ могк				
Parameter	g sol	as phase vent phase		Repor	ted data in gas phase	[Ref. 49].
					Bond (Å)	
1S - 3S	2.235	2.195	2.1	58	2.124	2.126
1S = 2O	1.506	1.508	1.4	99	1.486	1.488
3S – 4C	1.846	1.860	1.8	24	1.830	1.831
1S – 12C	1.868	1.868	1.0	83	1.839	1.834
4C – 6H	1.100	1.091	1.0	93	1.090	1.089
4C – 5H	1.090	1.089	1.0	91	1.093	1.089
206H	2.132	3.407	2.211		2.283	2.285
205H	3.642	4.335				
4C 2O	2.996	3.851	2.923		2.943	2.945
Angles (°)						
4C – 6H2O	133.39	105.85	120	.55	122.65	117.1
2O = 1S - 3S	107.38	110.72	107	.88	107.97	107.6
2O = 1S - 12C	104.88	106.15	105	.43	105.41	104.90
1S - 3S - 4C	97.78	98.10	96.	74	99.08	98.3
Dihedral (°)						
$\frac{12C - 1S - 3S}{-4C}$	92.09	155.66	87.	19	83.53	87.6
4C - 6H2O = 1S	9.814	35.12	21.	29	8.85	23.76

Table 6. Calculated selected geometrical parameters after optimization and comparison with reported data.

3.6.2 Global and Local Chemical Reactivity.

Another goal in this theoretical analysis was the calculation of the most relevant molecular properties and its effect on the Allicin chemical reactivity. These properties were: the dipole moment, ionization potential (IP), electron affinity (EA) and the global hardness (η). These parameters could give valuable information about the reactive behavior of the system (seetable 7).



Figure 15: Location of the HOMO orbitals for Allicin in a) gas and b) aqueous phase.



Figure 16: Location of the LUMO orbitals for Allicin in a) gas and b) aqueous phase

The local reactivity has been analyzed by means of the condensed Fukui functions [50, 51], since they indicate the reactive regions in the form of the nucleophilic and electrophilic behavior of each atom in the molecule. For the calculation of ionization potential (IP), electron affinity (EA) and the global hardness (η) next equations were applied:

$$E(N = N_0 - 1) - E(N = N_0) = IP$$
(10)

(11)

$$E(N = N_0) - E(N = N_0 + 1) = EA$$

$$\eta = \frac{1}{2} (I - A) \tag{12}$$

where $E(N = N_0 - 1)$ and $E(N = N_0 + 1)$ are the total electronic energies of the cationic and anionic species respectively, while the $E(N = N_0)$ is the total electronic energy of the neutral specie of the Allicin. The condensed Fukui functions (IF) are found by taking the finite difference approximations from Mülliken population analysis of atoms in molecules, depending on the direction of the electron transfer:

$$f_k^+ = q_k(N+1) - q_k(N) \qquad (for nucleophilic attack) \qquad (13)$$

$$f_k^- = q_k(N) - q_k(N-1)$$
 (forelectrophilicattack) (14)

$$f_k^0 = \left[q_k(N+1) - q_k(N-1)\right]/2 \qquad \text{(for radical attack)} \tag{15}$$

The HOMO energy (E_{HOMO}) can indicate the disposition of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals. Also an increase in the values of E_{HOMO} can facilitate the adsorption and therefore the inhibition efficiency [48]. On the other hand, the LUMO energy (E_{LUMO}) indicates disposition of the molecule to accept electrons The obtained values for E_{HOMO} present no significant differences as calculated in gas and solvent phase(see table 7).Since the E_{LUMO} values were less negative than those for E_{HOMO} , table 7, it indicates that Allicin has a greater tendency to donate electrons rather than to accept them. As can we see in table 7, the obtained value for the dipole moment (μ) in solvent (aqueous) phase (4.33 Debyes) is twice that in gas phase (2.51 Debyes).It is important to mention that μ is another way to obtain data about the electronic distribution in a molecule and it is traditionally one of the most used property to discuss and rationalize the structure and reactivity of many chemical systems [48]. On the other hand, the obtained results for the electron affinity (EA) show very different values in gas and solvent phase, being a positive value when water is present in the calculations.

Table 7. Molecular properties of Allicin calculated in gas and aqueous (solvent) phases.

Allicin	E _{HOMO} (eV)	Dipole Moment (Debye)	Total energy (neutral) (a.u.)	Total energy (cationic) (a.u.)	Total energy (anionic) (a.u.)	Ionization Potential (eV)	Electron Affinity (eV)	global hardness (eV)
gas phase	-6.57	2.51	- 1106.3107	- 1106.0027	- 1106.3102	0.3080	-0.0005	0.1542
solvent phase	-6.90	4.33	- 1106.3215	- 1106.0675	- 1106.3857	0.2540	0.0642	0.0949

The EA of an orbital is the energy released when the virtual (or a half-occupied) orbital accepts an electron, hence, when the accepted electron is bound the value of the EA in a molecule is positive [52-54]. In the same way, the global hardness shows a decrease when the solvent is present, it could be an indicative that the Allicin molecule increases its chemical reactivity when water is added.

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A most complete examination about the local reactivity of the Allicin was done by the application of Fukui indexes for each one of the atoms in the molecule. An analysis of the Fukui indexes along with the global hardness (η) could provide a more complete scheme of the local reactivity in the Allicin molecule. For simplicity, only the charges and Fukui functions over the oxygen (2O) and sulfur (1S y 3S) atoms are shown since these ones presented the most important sites for the electrophilic attack. An analysis of the Fukui indexes was performed with the Mülliken atomic charges distribution is shown in table 8. In this analysis only the largest values are presented. It is possible to observe that in gas phase, the sulfur atom (3S) is the most susceptible site for electrophilic attacks showing a value of 0.2808, while in solvent (aqueous) phase this site is shared with the oxygen atom (2O) which is the atom with the highest value, 0.2898. It is important to mention that the electrophilic attack (f_{-k}) measures the change of density when the molecule losses electrons by the reaction with cationic species, and it is probably the main interaction between the metallic surface and Allicin acting as a corrosion inhibitor molecule. When the Allicine molecule is adsorbed on the metallic surface, a coordinated bond is formed between this surface and the lone pairs of electrons present in the oxygen and sulfur atoms of Allicin via electron transfer.

Phase	Atom	q_N	q_{N+1}	q_{N-1}	f^{+}_{k}	f_k	$f^0_{\ k}$
	1S	0.6244	0.4707	0.7186	0.1538	0.0942	0.1240
Gas	20	-0.5285	-0.6188	-0.4102	0.0903	0.1183	0.1043
	3S	-0.0650	-0.3844	0.2158	0.3195	0.2808	0.3001
	1S	0.6277	0.4002	0.7683	0.2275	0.1407	0.1841
Solvent	20	-0.5965	-0.6832	-0.3067	0.0867	0.2898	0.1883
	3S	-0.0674	-0.4512	0.1234	0.3837	0.1908	0.2873

Table 8. Calculated Mülliken atomic charges and Fukui functions for the Allicin molecule calculated in gas and solvent (aqueous) phases.

Conclusions

A study of the use of Allicin as corrosion inhibitor for 1018 carbon steel has been carried out. Results have shown that Allicin is a good corrosion inhibitor, with its efficiency increasing with an increase in its concentration up to 400 ppm, but decreasing with a further increase in its concentration. Inhibitor efficiency decreased with an increase in the testing temperature because of the Allicin decomposition. The adsorption of Allicin on to the steel improves as time elapses until a certain period of time after which it starts to desorb from the steel surface. This inhibitor adsorption is also enhanced by increasing the steel rotating speed, which enhances the inhibitor presence at the metal surface. Theoretical calculations showed that Allicin can be adsorbed as molecular species using oxygen and sulfur atoms as active centers. Analysis of E_{LUMO} and E_{HOMO} values have shown than Allicin has a great tendency to donate electrons. The relationship between Allicin efficiency and its electronic properties were calculated and discussed.

References

- 1. Qiu L.G., Wu Y., Wang Y.M., Jiang X., Corros. Sci. 50 (2008) 576.
- 2. Abiola O.K., James A.O., Corros. Sci. 52 (2010) 661.
- 3. Cao P.G., Yao J.L., Zheng J.W., Gu R.A., Tian Z.Q., Langmuir 18 (2002) 100.
- 4. Osman M.M., Shalaby M.N., Mater. Chem. Phys. 77 (2003) 261.
- 5. El Ouasif L., Merini I., Zarrok H., El ghoul M., Achour R., Guenbour A., Oudda H., El-Hajjaji F., Hammouti B., *J. Mater. Environ. Sci.* 7 (8) (2016) 2718-2730.
- 6. Martinez D., Gonzalez R., Montemayor K., Juarez-Hernandez A., Fajardo G., Hernandez-Rodriguez M.A.L., *Wear* 267 (2009) 255.
- 7. Khan Ghulamullah, MdKazi, Newaz Salim, Basirun WanJefrey, Ali Hapipah BintiMohd, Faraj Fadhil Lafta, KhanGhulamMustafa, *Int. J. Electrochem. Sci.* 10 (2015) 6120.
- 8. Anupama K.K., Ramya K., Shainy K.M., Joseph Abraham, Mater. Chem. Phys. 167 (2015) 28.
- 9. HazwanHussin M., Abdul RahimAfidah, Ibrahim Mohamad Nasir Mohamad, Brosse Nicolas, *Mater. Chem. Phys.* 163 (2015) 201.
- 10. ZhangBingru, HeChengjun, Wang Cheng, SunPeidi, LiFengting, Lin Yu, Corros. Sci. 94 (2015) 6.
- 11. Ji Gopal, AnjumShadma, SundaramShanthi, Prakash Rajiv, Corros. Sci. 90 (2015) 107.

- 12. Ngobiri N. C., Oguzie E. E., Li Y., Liu L., Oforka N. C., Akaranta O., Int. J. Corrosion, 2015 (2015) 9 pages
- 13. El Hamdani N., Fdil R., Tourabi M., Jama C., Bentiss F., Appl. Surf. Sci. 357 (2015) 1294.
- 14. Rajeswari Velayutham, Kesavan Devarayan, Gopiraman Mayakrishnan, Viswanathamurthi Periasamy, Poonkuzhali Kaliyaperumal, Palvannan Thayumanavan, *Appl. Surf. Sci.* 314 (2014) 537.
- 15. Rietz B., Isensee H., Strobach H., Makdessi S., Jacob R., Mol. Cell. Biochem. 119 (1993) 143.
- 16. Isensee H., Rietz B., Jacob R., Drug Res. 43 (1993) 94.
- 17. Arora R.C., Arora S., Gupta R. K., Atherosclerosis, 40 (1981) 175.
- 18. Curtis Hannah, Noll Ulrike, Stormann Judith, Slusarenko Alan J., Physiol. Mol. Plant Pathol. 65 (2004) 79.
- 19. Benkeblia N., Lebensm.-Wiss. u.-Technol. 37 (2004) 263.
- 20. Ankri Serge, Mirelman David, Microb. Infect. 2 (1999) 125.
- 21. Bakri I.M., Douglas C.W.I., Arch Oral Biol. 50 (2005) 645.
- Oommen Suby, John Anto Ruby, Srinivas Gopal, Karunagaran Devarajan, Eur. J. Pharmacol. 485 (2004) 97
- 23. Hirsch Keren, Danilenko Michael, Giat Judith, Miron Talia, Rabinkov Aharon, Wilchek Meir, Mirelman David, Levy Joseph, Sharoni Yoav, *Nutri. Cancer* 38 (2000) 245.
- 24. Block E., Angew. Chem. 31 (1992) 1135.
- 25. Agarwal K.C., Med. Res. Rev. 16 (1996) 111.
- 26. Bakht J., Tayyab M., Ali H., Islam A., Shafi M., Afr. J. Biotechnol. 10 (2011) 5910.
- 27. Becke A.D., J. Chem. Phys. 98 (1993) 5648.
- 28. Stephens P.J., Devlin F.J., Chabalowski C.F., Frisch M.J., J. Phys. Chem. 98 (1994) 11623.
- 29. Kimbaris A.C., Siatis N.G., Pappas C.S., Tarantilis P.A., Daferera D.J., Polissiou M.G., *Food Chem.* 94 (2006) 287.
- 30. Lanzotti V., J. Chromatogr. A, 1112 (2006)3.
- 31. Block E., Naganathan S., Putman D., Zhao S.H., J. Agric. Food Chem. 40 (1992) 2418.
- 32. Han J., Lawson L., Hand G., Han P., Anal. Biochem. 225 (1995) 157.
- 33. Amagase H., Petesch B.L., Matsuura H., Kasuga S., Itakura Y., J. Nutrition 131 (2001) S955.
- 34. Chipiti T., Ibrahim M.A., Koorbanally N.A., Islam S., *Acta Polytech. Scand., Chem. Technol. Ser.* 72 (2015) 119.
- 35. Solmaz R., Sahin E.A., Doner A., Kardas G., Corros. Sci. 53 (2011) 3231.
- 36. Özcan M., Dehri I., Erbil M., Appl. Surf. Sci. 236 (2004) 155.
- 37. Solmaz R., Kardas G., Culha M., Yazıcı B., Erbil M., Electrochim. Acta 53 (2008) 5841.
- 38. Poorqasemi E., Abootalebi O., Peikari M., Haqdar F., Corros. Sci. 51 (2009) 1043.
- 39. Poornima T., Nayak J., Shetty A.N., J. App. Electrochem.41 (2011) 223.
- 40. Solomon M.M., Umoren S.A., Udosoro I.I., Udoh A.P., Corros. Sci. 52 (2010) 1317.
- 41. Obot I.B., Obi-Egbedi N.O., Eseola A.O., Ind. Eng. Chem. Res. 50 (2011) 2098.
- 42. Okada Y., Tanaka K., Sato E., Okajima H., Org. Biomol. Chem. 4 (2006) 4113.
- 43. Hilal R., Abdel Khalegh A. A., Elroby S. A. K., Int. J. Quant. Chem. 103 (2005) 332.
- 44. Oguzie E.E., Li Y., Wang F.H., J. Colloid Interface Sci. 310 (2007) 90.
- 45. Branzoi V., Branzoi F., Baibarac M. M., Mater. Chem. Phys. 65 (2000) 288.
- 46. Ahamad I., Quraishi M.A., Corros. Sci. 52 (2010) 651.
- 47. Oguzie E.E., Li Y., Wang F.H., J. Colloid Interface Sci. 310(2007) 90.
- 48. Branzoi V., Branzoi F., Baibarac M. M., Mater. Chem. Phys. 65(2000) 288.
- 49. Khalil N., Electrochim. Acta 48 (2003) 2635.
- 50. Rodríguez-Valdez Luz María, Villamisar W., Casales M., González-Rodriguez J.G., Martínez-Villafañe Alberto, Martinez L., Glossman-Mitnik Daniel, *Corros. Sci.* 48 (2006) 4053.
- 51. Durlak Piotr, BerskiSławomir, LatajkaZdzisław, Chem. Phys. Letters 644 (2016) 5.
- 52. Lee C., Yang W., Parr R.G., J.Mol.Struct. (Theochem) 163 (1988) 121.
- Rodríguez-Valdez L.M., Martínez-Villafañe A., Glossman-Mitnik D., J. Mol. Struct. (Theochem) 713 (2005) 65.
- 54. Lowe J. P., Quantum Chemistry, Klumer Academic Publishers, (2004).

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