4-Hydroxy-3,5-dimethoxybenzaldehyde as "green" corrosion inhibitor for copper: Experimental and theoretical approaches

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As one of the simplest, convenient for applications, and efficient methods of the corrosion protection of the metal products under the conditions of atmospheric corrosion (AC), we can mention the application of volatile inhibitors [1-3]. Due to the more strict environmental regulations that have been implemented in recent years, corrosion inhibitors are required to have an environmentally friendly profile. Due to these concerns, green coatings have been a new trend in corrosion protection and extensive study is necessary to understand the mechanism of the coatings. In view of the ecological requirements and the lack of the major part of high-performance VIAC, it was decided [3] that natural compounds of vegetable origin can be regarded as promising raw materials for the production of inhibitors of this kind. The increasing trend of number of published papers regarding copper corrosion inhibitors in recent years shows the importance of this issue for researchers [3, 4]. As one of these sources, we can use the rapeseed oil cake (from the *Brássica Nápus* family) [5, 6]. As shown in [7], the 2-propanol extract of volatile compounds of the rapeseed oil cake provides an efficient protection of cooper against AC under the conditions of periodic condensation of moisture for 20 days. In analyzing the chemical composition of the 2-propanol extract with the help of gas-chromatography–mass spectrometry, it was shown that its main constituents is syringaldehyde (4-Hydroxy-3,5-dimethoxybenzaldehyde). Was shown in the course of AC, the adsorption of organic compounds of extract takes place both on the surface of the metal and on the products of its oxidation and, in order to explain the mechanism of protective action of the

organic compounds, one can use the concept of resonance potentials [7]. The comparison of the resonance potentials of copper and its main compounds with the ionization potentials of the main organic components of the extract shows that syringaldehyde (4-Hydroxy-3,5-dimethoxybenzaldehyde) is characterized by higher adsorption activities to the oxidized surfaces. Then, in view of the ability of copper to form chemical compounds, adsorption transforms into chemisorption. Also organic compounds containing conjugated double bonds, several heteroatoms (i.e. sulfur, nitrogen, oxygen) and/or polar functional groups generally exhibit favorable inhibitive properties, so they can always be employed as inhibitor for corrosion of copper [7]. Quantum theoretical calculations have been used by many researchers to establish the mechanistic information on corrosion and inhibition process [4-6]. Despite that in our previous work we have already theoretical explored some adsorption phenomenon of the main components as inhibitors through principle the calculated ionization potentials [7, 8]. However, information about the inhibition mechanism of syringaldehyde from the theory aspect remains unanswered. The application of the concept of resonance potentials is most rigorously substantiated for the interpretation of the chemisorption of surface-active substances (SAS) for which physical adsorption have a minor significance. If adsorption is caused by the electrostatic forces, especially in the case of adsorption of SAS on the metals with high negative corrosion potentials, then this concept does not explain the efficiency of action of the SAS. Therefore, it is expedient to study theoretically adsorption ability of a substance, both physical and chemical, using quantum chemical calculations. Considering the above information and with the purpose of attaining an effective eco-friendly corrosion inhibition treatment avoiding the addition of the inhibitor to the surrounding environment, the evaluation of syringaldehyde is reported here. Syringaldehyde is aromatic aldehyde derivative component of different types of plant raw materials. Thus, the aim of this work is to elucidate inhibitory effect of syringaldehyde as a green volatile corrosion inhibitor copper and protective characteristics of the layers formed on copper.

2. Experimental

2.1. Materials and Apparatus

To study the efficiency of its action upon the corrosion-electrochemical behavior of copper, we used specimens made of M0 copper (99.95% Cu). Syringaldehyde which chemical structure is shown in Fig. 1 was used in the experiments. The inhibitor used was syringaldehyde (4-Hydroxy-3,5-dimethoxybenzaldehyde) with the concentration range from 50 to 300 mg/L.
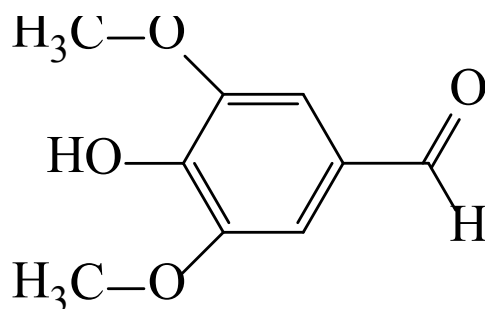

Fig. 1. Chemical structures of syringaldehyde (4-Hydroxy-3,5-dimethoxybenzaldehyde).

The purity is 99.0% on dries basis dissolution of syringaldehyde was directly carried out in solution 2-propanol at room temperature and used as volatile corrosion inhibitor in all the experiments.

2.2. Gravimetric measurements

Volatile inhibiting sieve test were applied to evaluate the inhibition effect of the VIAC. To obtain reproducible results three samples were used in each test simultaneously. There was a hole in each plate drilled to suspend the sample by a nylon thread. The samples were grinded with SiC paper to 1000 mesh and were then cleaned in alcohol and rinsed before drying at room temperature. The final geometrical area was 25 cm^2. The gravimetric measurement was conducted by suspending the samples in a 250 cm^3 conical flask with a tight-fitting rubber cork containing a small dish. The VIAC were dispersed in the dish. The samples with freshly prepared surface were mounted on the flask with and without 1.0 g inhibitor, respectively. After inhibitor film-forming period of 3 days, 15 cm^3 0.01 M NaCl was added. The test process included cyclic warming and cooling of the samples in a corrosion testing chamber of varying humidity. One cycle included an 8 h exposure

in the thermostat (50 ± 1°C), and 16 h exposure at room temperature. The total duration of the tests was 21 days. The efficiency of inhibitors was estimated according to the degree of protection against corrosion (IE) [7, 8].

2.3. Electrochemical measurements

To determine the influence of protective surface films on the cathodic and anodic electrode AC processes for copper, we plotted the potentiodynamic polarization curves for a three-electrode electrochemical cell in air by separating the anolyte from the catholyte (the volume of working solution was 60 cm ^{3}). We used a cylindrical copper electrode pressed into a Teflon holder and a platinum plate as an auxiliary electrode. The disk end face of the copper electrode 0.385 cm^2 in area served as the working surface. We plotted the polarization curves in a 0.01 M NaCl solution used to model the aggressive medium of the AC of metals [2]. As a specific feature of our electrochemical investigations, we can mention the following fact: the disk-shaped surface of the end face of the working electrode was immersed in surface layers of the working solution by at most 1–2 mm. This enabled us to perform more exact modeling of the AC running on the metal surface in thin layers of condensed moisture. A capillary from the reference electrode was placed near the surface of the working electrode from below. Prior to processing in the VIAC vapor, the working electrode was polished and degreased with acetone. The VIAC film on the surface was preliminarily formed in vapors of the syringaldehyde. The polarization investigations were performed by using a PI-50-1.1 potentiostat and a PR-8 programmer. The potential of copper was measured relative to the silver-chloride reference electrode. The induced electrode potentials were recalculated relative to the normal hydrogen electrode.

The electrochemical impedance spectroscopy (EIS) was measured atopen circuit potential with a 10 mV AC perturbation at frequency ranging from 100 kHz to 0,05 mHz with 10 points per decade. The testdevice and the cell configuration for the EIS measurements werethe same as those for the polarization curve tests.To prove reproducibility, the polarization curve tests and the EIS measurements were repeated three times.

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2.4. Scanning electron microscope (SEM)

The morphologies of the metal surfaces of the specimens without films and after the formation of the VIAC film and corrosion tests were studied with the help of a by FEI E-SEM XL 30. For SEM images, 1cm^2 specimen sample were taken.

2.5. Quantum chemical calculations

According to the literature data [4-6,9-10], the adsorption activity of organic molecules and, hence, their susceptibility to chemisorption can be estimated by the reactivity indices, various electronic structure parameters obtained as a result of quantum-chemical calculations with regard for the electronic and energy characteristics of the inhibitor and the metal. Therefore, a prognostic estimate of the adsorption capacity based on the electronic characteristics of molecules such as the energy of the higher occupied molecular orbital (E *HOMO*) and the energy of the lower vacant molecular orbital (E *LUMO*), the energy of the molecular gap ($\Delta\varepsilon$ =E($_{HOMO}$) - E($_{LUMO}$)) was carried out, electronegativity and chemical hardnessof a molecule based on the theory of functional density. It has been established that corrosion inhibitors usually promote the formation of a chelate on the metal surface, which include the transfer of electrons from the organic compounds to the metal, forming a donor-acceptor bond during the chemical adsorption process. According to *Koopman's* theorem [4-6], the frontier orbital energies E_{HOMO} and E_{LUMO} are related to the ionization potential, I, and the electron affinity, A, of iron and the inhibitor molecule by the following relations: A $=-E_{LUMO}$, I $=-E_{HOMO}$.

In this adsorption, the metal acts as an electrophile while the inhibitor acts as a nucleophile. Considering the charge transfer characteristics of the adsorption, the wide use of quantum chemical calculations to study this process is justified. Calculated electron charges on the atoms of molecules were determined by their ability to chemical interaction and by the wave function of the HOMO and the LUMO, the most probable adsorption centre and the predictive adsorption capacity of the compounds were determined. In addition, it is known that the more a negative charge on a heteroatom, the better the transfer of electrons from the donor occurs. Taking into account the characteristics of the transfer of charge of adsorption, the

literature substantiates the widespread use of quantum-chemical calculations for the study of this process [4-6, 9-10]. *Pearson* and *Parr* were presented definitions using the finite differences method depending on electron affinity (A) and ionization energy (I) of any chemical species (atom, ion or molecule) for chemical hardness (η), and chemical potential (χ) According to the theory of functional density, the absolute electronegativity (χ), chemical potential (μ) are the main parameters that characterize the ability of molecules to chemically interact. The chemical potential, electronegativity, chemical hardness of an electronic system is defined as detailed in the works [4-6,9-10].

$$\chi = -\mu = \frac{1}{2}(I+A)$$
(1)

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

The global electrophilicity index (ω) was introduced by *Parr et al.* [8, 9] and is given by:

$$\omega = \frac{(I+A)^2}{8(I+A)}$$
(3)

In considering the adsorption process from the point of view of the acid-basic interaction, the important quantitative parameters characterizing this process are the degree of charge transfer ΔN, that is, the interaction strength of acid-acceptor molecules (iron surface) and the donor base (investigated substances of the vapor phase of the extract) and the magnitude of the energy change that accompanies the formation of the complex. The electron charge transfer, ΔN, from base B to acid A, and the associated energy change ΔE is given as:

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A + \eta_B)}$$
(4)

$$\Delta E = \frac{(\mu_B - \mu_A)^2}{2(\eta_A - \eta_B)}$$
(5)

$\chi = -\mu$ – electronegativity, eV;

η- chemical hardness, eV;

A, B - Indices in formulas (4,5);

A - characteristics of the molecule of the test substance;

B - characteristics of the elemental lattice of the surface of iron.

The electronegativity of metal surface is replaced by the work function for Fe (110) surface, theoretically equals 4.82 eV and the hardness metal which equals 0 eV for bulk metals [8,9].

Quantum chemical calculations have been performed by the HyperChem 7 package. The geometry optimization was obtained by application of the restricted Hartree-Fock method (RHF) using MNDO approach with PM3 parameterization.

These parameters will provide insights into the mechanism of the interaction of the extract components with mild steel surface.

3. Results and discussion

Corrosion rate and inhibition effectiveness for the test samples are shown in Tabl. 1.

Table 1. Calculated corrosion rates and inhibition efficiency for volatile corrosion inhibition test VIAC (Period of film-forming, 48 h, conditions of periodic condensation of moisture (0.01 M NaCl for 21 Days).

Concentration inhibitor, mg/L	Corrosion rates, g /m^{-2} h^{-1}	Inhibition efficiency (IE), %
50	0.001514	48.14
100	0.000429	85.30
150	0.000327	88.79
200	0.000202	93.08
250	0.000105	96.41
300	0.000049	98.33
without inhibitor	0.002920	-

The analysis of the results of accelerated corrosion tests shows that the syringaldehyde protect copper from corrosion under the conditions of periodic

moisture condensation. The corrosion rate and inhibition effectiveness for the syringaldehyde film-forming specimens were and 98.33%, respectively. It should be noted that the treatment of specimens in the vapor phase of individual 2-propanol does not improve the corrosion resistance of the metal.

It was investigated the effect of exposure time of the metal on the vapour phase of syringaldehyde on corrosion effect under the conditions of periodic moisture condensation. The exposure time was varied between 5 and 72 h (Fig. 2). It should be noted that the corrosion rate to decreases with increasing the time film formation [1, 6-7]. The inhibition efficiency (IE) increases in the range 37.06-98.25%. The corrosion inhibition efficiency values for syringaldehyde corrosion inhibitors after 5, 12, 24, 48, 72 h are obtained 37.91%, 84.29%, 87.84%, 97.24% and 98.25%, respectively are shown in Figure 2.
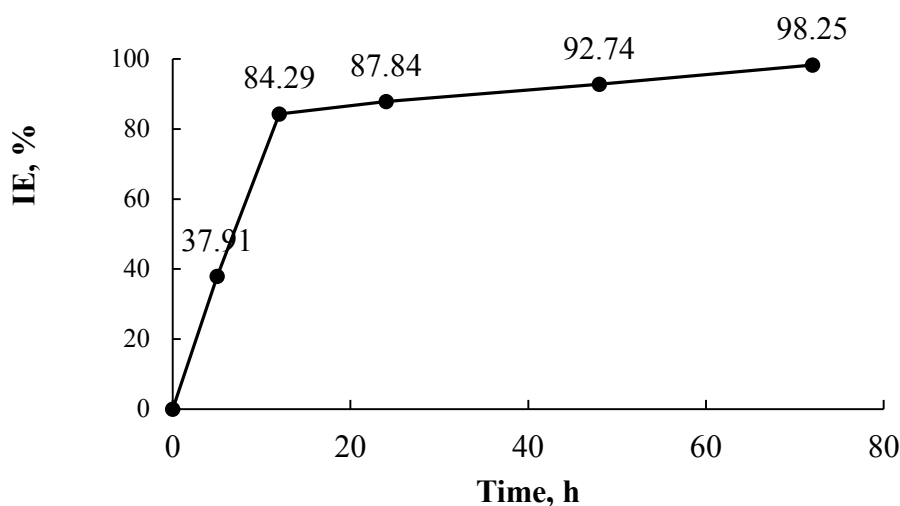

Fig. 2. Inhibition efficiencies for copper under the conditions of periodic moisture condensation 0,01 M NaCl solution with different time film-forming.

3.2 Electrochemical Investigations of the Partial Electrode Processe.

In analyzing the influence of VIAC films on the rate of the partial electrode processes of anodic oxidation of copper and cathodic reduction of the molecular atmospheric oxygen in a 0.01 M NaCl solution with and without protective films (Fig. 3).

If the VIAC films are present on the copper surface causes a considerable decrease in electrochemical reactions the rate of the anodic and cathodic processes, although their effects on decreasing anodic dissolution of copper are more dominant. In the presence of a VIAC film on the copper surface, the anode current density sharply decreases, especially under the potential equal to 0.35 V. Almost equal anode current densities in the course of passivation of copper under a potential of 0.8 V in the no matter how long the film is formed on the surface are usually explained by the fact that, under these conditions, the rate of dissolution of the metal is determined not by the protective characteristics of the film but by the properties of the layer of products of the dissolution of copper. It may happen that, for high degrees of polarization, the film may lose its integrity or disappear from the surface. As the time of treatment of the metal by the volatile compounds of syringaldehyde increases to 48 h, the increase in the inhibiting efficiency becomes especially pronounced, which corresponds to the saturation of the surface with the inhibitor and the formation of the strongest bonds between the inhibitor and the metal.
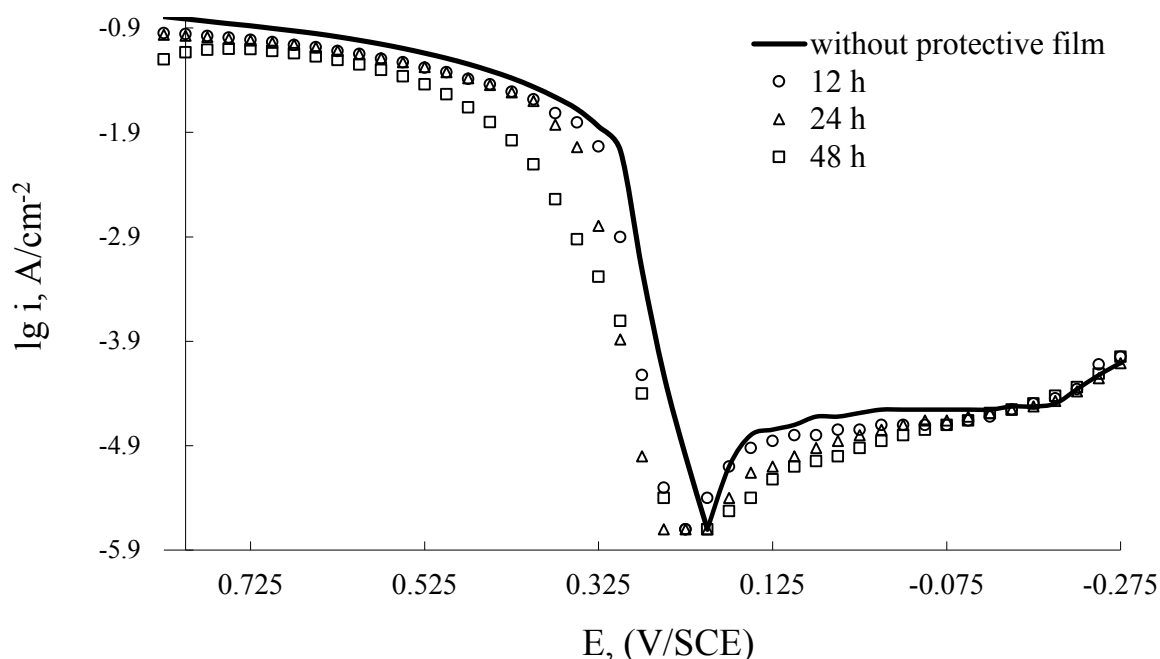

Fig. 3. Polarization cathodic and anodic curves of copper in a 0.01 M NaCl solution without (1) and with (2) the films of volatile inhibitors of atmospheric corrosion formed for 12, 24, 48 h in the vapor phase of the syringaldehyde.

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The changes in the slopes of the curves of anodic polarization after 48 h film-forming within the range of potentials between the maxima of anode current densities show that the formation of surface compounds is controlled by different stages. Moreover, the nature of controlling stage most clearly changes in the presence of a film on the surface. Since the rate of anodic processes of the dissolution of copper both in the absence and in the presence of the surface film is much higher than the rate of cathodic processes, it is possible to assert that the film does not change the nature of the controlling partial process of the corrosion of copper in thin interlayers of the 0.01 M NaCl solution. In other words, under the conditions of AC, the dissolution of copper is controlled by the cathodic process.

The effect of corrosion inhibitor on both anodic and cathodic branches implies to mix nature of corrosion inhibitor, although anodic reaction is more influenced.

The Nyquist diagrams (Fig. 4) obtained without inhibitor (blank) and with the film that obtained after period of film-formed (12, 24, 48 h) in vapor phase of inhibitor shows a depressed semicircle in the high frequency region. This high frequency semicircle is mainly due to the charge transfer and double-layer capacitance [9]. For time film-forming of 12 and 24 h, and more particularly for 12 h, the shape of the diagram in the high frequency region differs and appears to involve two overlapping semi-circles. The second semi-circle may correspond to the film of corrosion products. For time film-forming 48 h, a slight inductive behavior is observed at low frequency. It could be linked to a non-stationarity of the system. However, the evolution of open-circuit potential (OCP) was followed with time (results not shown) and it was observed that in any case, the OCP was stable after less than 15 minutes. Consequently, such a behavior may rather be due to adsorption phenomena and thus may point out the chemosorption of the inhibitor on the copper surface.

This inductive behavior was neglected, i.e. the data corresponding to the highest frequencies of this peculiar impedance diagram were excluded for the modelling. Actually it is masked by a stronger effect at the higher time film-forming 12 and 24 h. For these two period of film-formed and for the blank as well, the curves deviate from their semicircular shape at low frequency, which may be related to a diffusion

phenomenon, more likely that of dissolved O_2. From the analysis of the potentiostatic polarization curves, it was deduced that O_2 reduction was under mixed activation-diffusion control after 12 and 24 h period of film-forming and mainly under activation control after 48 h. In the case of the blank solution, both situations were met and the Nyquist plot shown here corresponds to a case where the cathodic reaction was partially controlled by diffusion. In accordance with this preliminary description of the EIS results, the analysis of impedance data were performed with the various equivalent circuits presented in Figure 5.
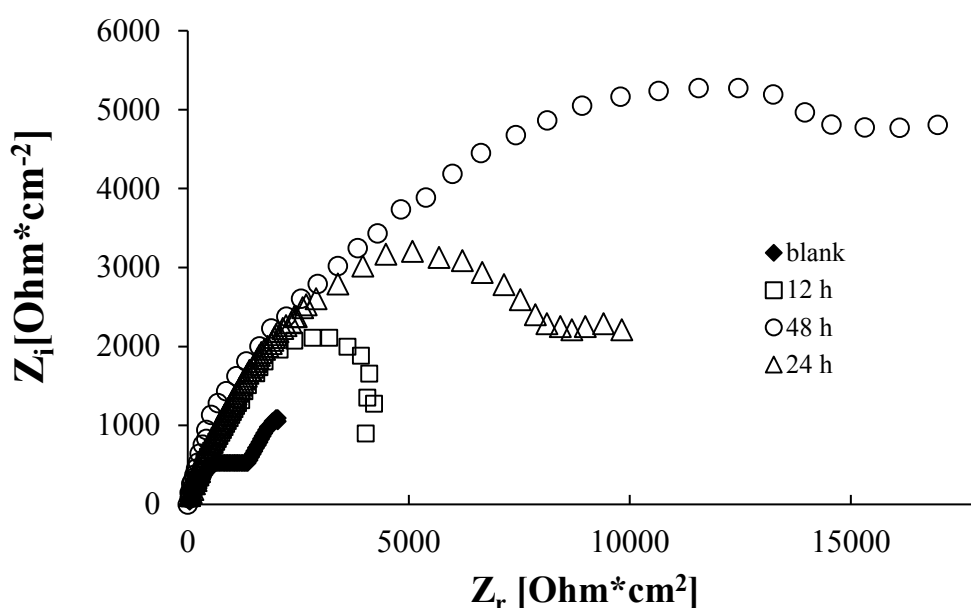

Fig. 4. Nyquist plots for copper electrode immersion in 0.01 M HCl solutions without (blank) and with various time of film-forming (12, 24, 48 h) of syringaldehyde.
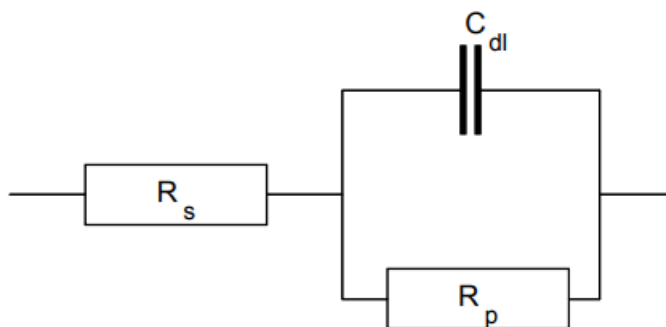

Fig. 5. Equivalent circuits for test copper

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Table 2. Electrochemical impedance parameters obtained for concentration 300 mg/L after various times compared to those obtained without inhibitor

Time (h)		R_s	R_p	Q_{dl} 10^{-3}	W	IE
Blank (after 24 h of exposure in the air)		8.5	2500	0.15	216	-
With inhibitor	12	8.4	8940	0.14	434	73,2
	24	7.8	13300	0.11	110	72,8
	48	6.6	22000	0.07	334	91

*W - resistance of Warburg, which is connected with diffusion limitation (resistance of electrolyte in pores)

These models were used in various studies to describe the behavior of copper or copper alloys in chloride containing solutions, with or without adsorption inhibitors [8, 9]. That of Figure 4proved suitable for the Nyquist plot of copper in the blank solution. In this model, Rs is the solution resistance, R_p is the charge transfer resistance, Q_{dl} corresponds to the capacitance of the double layer and W is the Warburg impedance related to the diffusion processes in the low frequency region. This shows that the contribution of the film of corrosion products formed on the metal surface is negligible.

3.3 Scanning electron microscope (SEM) surface examination

The adsorption process due to the action of syringaldehyde was monitored with an SEM while varying the exposure time. The investigations of the morphology of copper surface prior to and after corrosion tests performed under the conditions of AC show that, on the surfaces of specimen without films, one can detect only traces of the mechanical processing of the surface (Figure 6 a). The following images (Figure 6 b, c) are of the copper surface after 24, 35, 48 h of exposure for the film-forming of the syringaldehyde. It shows a thin and covering surface film. After

holding of the specimens for 24 h in the vapor of syringaldehyde, a protective film (containing spherical inclusions whose diameter is several times larger than the thickness of the film) appears on the surface (Figure 6 b). Most likely, the formation of inclusions is connected with the fact that the syringaldehyde is primarily adsorbed in the oxidized domains (active centers).
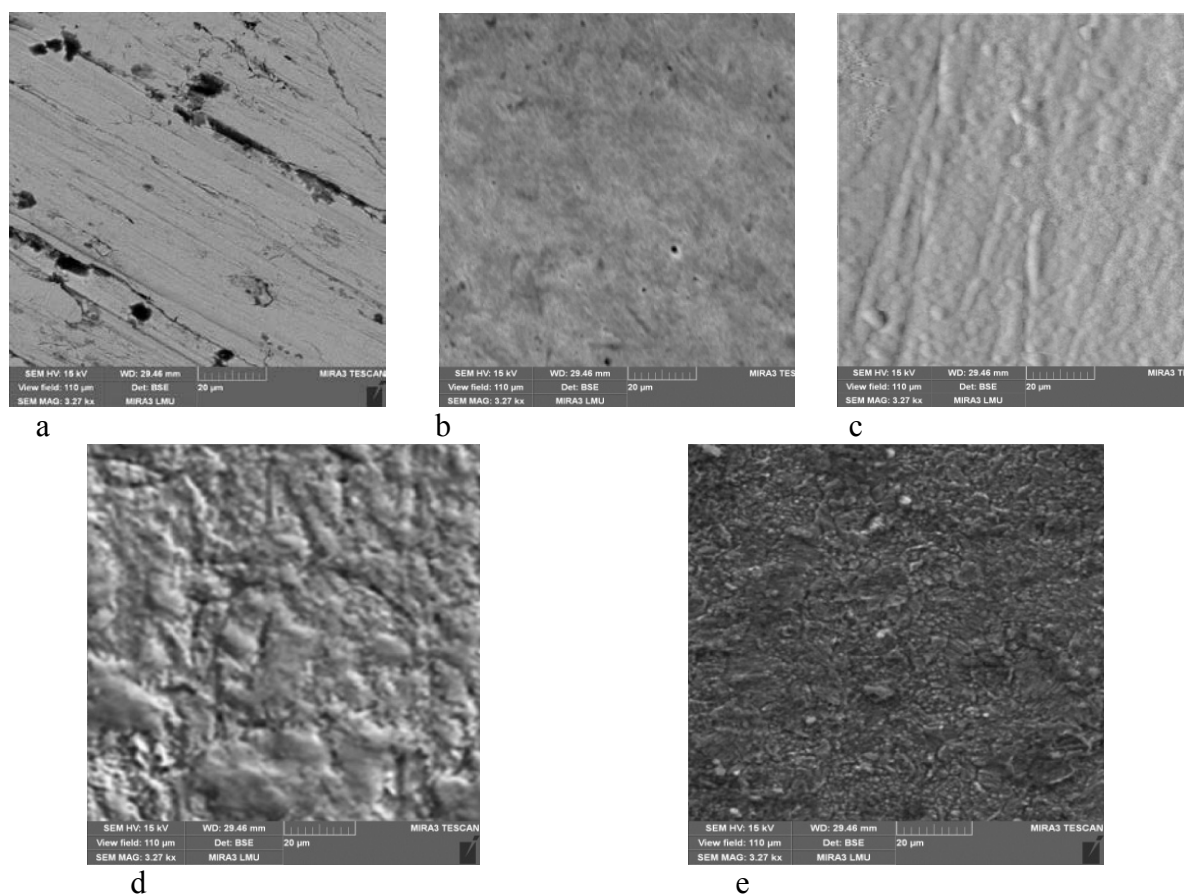

a   b   c

d   e

Fig. 6. Morphology of the surface of copper specimens: (a) after mechanical processing, after the formation of a film for 24, 35, 48 h (b, c, d) in the gas-vapor atmosphere in the presence of syringaldehyde, after cyclic tests for 21 days under the conditions of condensation of moisture (e) (0.01 M NaCl).

This organic compound is gradually transformed into chemisorbed compounds with copper ions responsible for the adsorption of the other compounds. Syringaldehyde adsorb on the copper surface with the contribution of both chemisorption and physisorption, although, chemical adsorption play more dominant role on corrosion inhibition. The presence of protective film considerably reduces the corrosion attacks through the formation of a protective layer which acts as a physical

barrier against aggressive ions. The bare copper in a corrosive medium showed a severe attack, whereas the layer formed copper showed a homogeneous and smooth surface without corrosion products. From the SEM image, it can be concluded that the films effectively protect the copper surface from corrosion. It was investigated the changes in the morphology of the surface films after the course of cyclic corrosion tests when the analyzed film is periodically wetted and dried. In the course of formation films after 48 hours, we observe the hydration of the film and its volume increases, i.e., the film swells. As temperature increases, the film gets dry, shrinks, and possibly, partially loses its integrity forming a film of the «shagreen type» (Figure 6 d), which results in worsening of its protective properties. This effect was observed and studied of the mechanism of action of the 2-propanol extract of Rapeseed oil cake on the atmospheric corrosion of copper [5].

3.4 Quantum theoretical studies

Accordingly, quantum chemical calculations are performed to investigates the structural parameters affect the inhibition efficiency of inhibitors; study their adsorption mechanisms on the surface and film forming process. The adsorption study regarding large size inhibitors are still relying on conventional molecular mechanics method (Fig. 7). The HOMO energy reflects the capacity of a molecule to donate electrons, whereas the LUMO energy corresponds to a tendency for electron acceptance [15-27]. The HOMO/LUMO energy gap ($\Delta\varepsilon$) for syringaldehyde was derived from the values E_{HOMO} = (-9.44 eV) and E_{LUMO} (-0.686 Ev) to be 8.75 eV. Low values of $\Delta\varepsilon$ imply that minimal energy will be required to remove an electron from the last occupied orbital, corresponding to an increase in metal/inhibitor chemisorptive (covalent) interactions, hence improved inhibition efficiencies.

Table 3. Calculated quantum chemical properties for the syringaldehyde.

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta\varepsilon$ (eV)	dipole moment (μ)
Syringaldehyde	-9.440	-0.686	8.754	5.4882

Figure 7 shows the electric/orbital density distribution of HOMO and LUMO for syringaldehyde. It is found that the electron density of the frontier orbital is well proportioned (Fig. 7). Such results indicate syringaldehyde could be both the acceptor of the electron and the donor of the electron. That is, there is electron transferring in the interaction between the inhibitor molecule and metal surface. Hence, the electrons might be inclined to transfer from the HOMO orbitals of syringaldehyde like molecules to copper surface. This has been further validated by the ΔN descriptor, since all the ΔN values listed in Table 4 are positive.

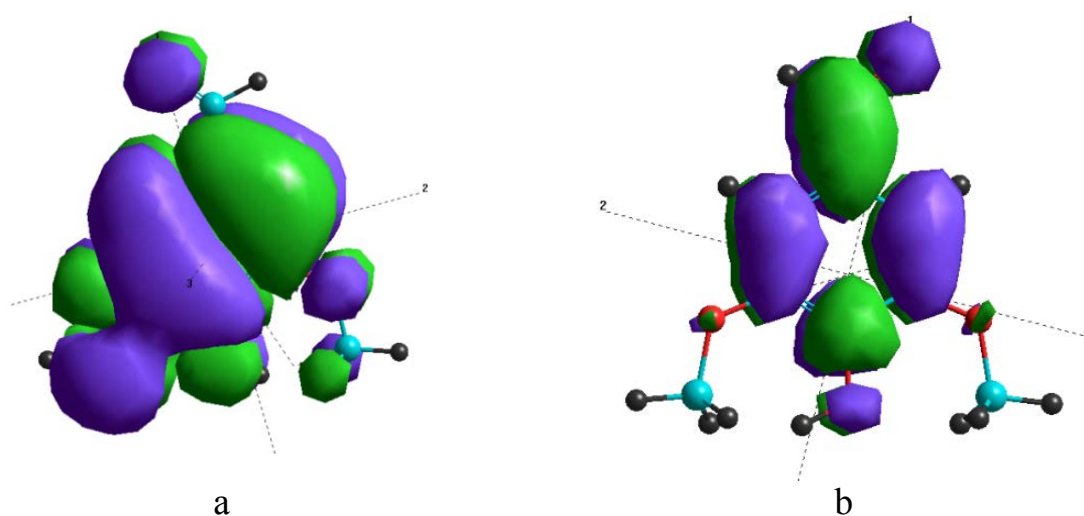a   b

Fig. 7. The frontier molecular orbital density distribution of syringaldehyde (a) HOMO and (b) LUMO.

We should declare that ΔN values do not represent accurately the number of electrons transferring between the donor and acceptor. Therefore, another expression "electron-donating ability" (abbreviated as EDA) may be more appropriate than "number of transferred electrons". The ΔN values determine the EDA of inhibitors (Table 4), and the bigger the ΔN value, the greater the EDA for one inhibitor molecule. Based on Lukovits's study [15-27], when $\Delta N < 3.6$, the inhibition performance improves with higher EDA.

Table 4. Calcultated quantum chemical properties for the syringaldehyde

Molecule	Ionization potential, (I)	Electron affinity (A)	Electronegativity (χ)	Hardness (η)	Softness (S)	Electrophilicity index (ω)	Nucleophilicity (ε)	ΔN
Syringaldehyde	9.44	0.686	5.063	4.37 7	0.228	1.25	0.8	0.221

We can also find that the optimized inhibitor molecules almost all show planar structures, and their frontier molecular orbitals are π-type, which suggest a parallel adsorption mode for the inhibitors on iron surface.

The reactive centers and the high electron density regions of molecules can be determined with the help of molecular ESP maps (Fig. 8b).

As is shown in Figure 3a, the electrostatic potential have been characterized with different colors, purple and green colors stand for the regions of the negative and positive electrostatic potential, respectively. It is evident from Figure 3 that the oxygen atom Carbonyl group has the majority of the negative charges. Therefore, it can be concluded that the aldehyde molecule can be absorbed physically by electrostatic forces.

a   b
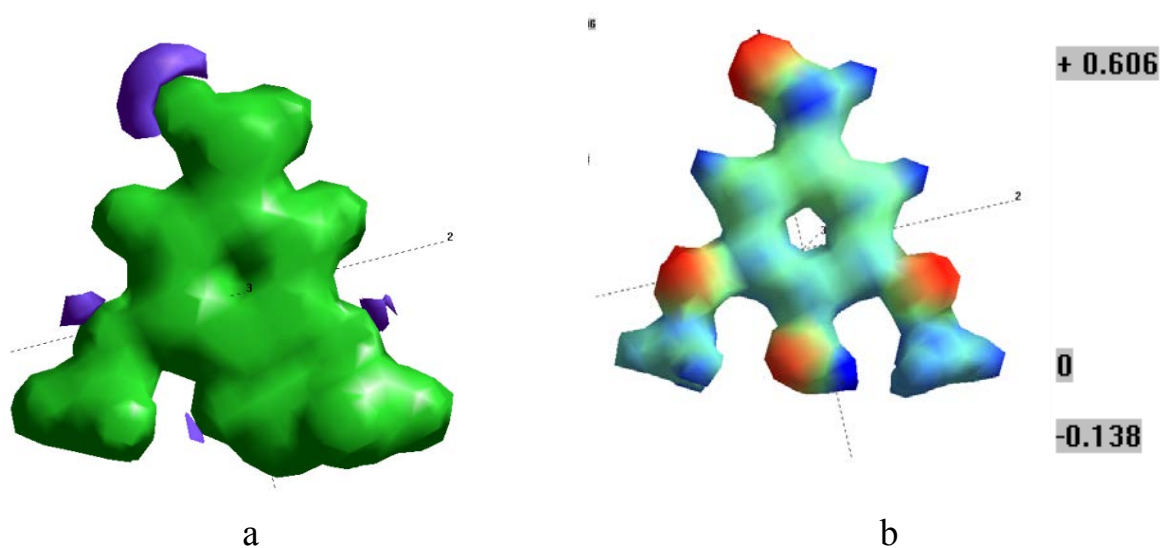
Fig. 8. Electrostatic potential (a) and 3d isosurface (b) representation of electrostatic potential structure for syringaldehyde.

Inspection of the data in Table 2 shows that the ΔE value of syringaldehyde is lower, which can facilitate its adsorption on the metal surface so it has higher inhibition efficiency. To obtain a clear picture of the interaction between the molecular of syringaldehyde and mild steel surface, intermolecular parameters such as a charge transfer descriptors and the associated energy change should be taken into account. Corrosion inhibition of mild steel syringaldehyde is a complex process and is mainly influenced by charge transport. Electrophilicity is an index which measures the propensity of chemical specie to accept electrons. The higher the value of ω, the higher the capacity of the molecule to accept electrons. Thus, a good nucleophile is characterized by low values of μ and ω; whereas a good electrophile is characterized by high values of μ and ω. It is clear in Table 2 that the molecules have low electrophilicity index values and are good nucleophiles. Electrophilicity may be stated as the measure of reactivity to-wards attracting electrons from a nucleophile of a chemical species. Nucleophilicity (ε) is physically in verse of electrophilicity (1/ω). For this reason, it should be stated that a molecule that have large electrophilicity value is ineffective against corrosion while a molecule that have large nucleophilicity value is a good corrosion inhibitor.

3.3 Mechanism of inhibition of syringaldehyde on copper corrosion

Thus, on the basis of experimental data and quantum chemical calculations the adsorption of organic molecules was not considered only as a physisorption adsorption or as a chemisorption adsorption. Due to the fact that syringaldehyde at interacted with the metal surface to inhibit the corrosion reaction, we can assume that the adsorption of syringaldehyde molecules was preferential chemisorption on the surface in combination with physisorption.

At the first stage occurs the physical adsorption of the vanillin due то electrostatic potential of molecule. In the second stage reaction centers are unshared electron pairs of heteroatoms and π-electrons of aromatic/heterocyclic ring. The organic molecules may adsorb on the metal/solution interface by one and/or more of the following ways: (1) donor-acceptor interactions between the π-electrons of aromatic rings and vacant d-orbital of surface copper atoms, and (2) interaction between unshared electron pairs

of hetero atoms and vacant d-orbital of copper surface atoms. These processes stipulate formation of aprotective film and drastically reduce the transport of aggressive ions to the metal surface thereby controlling the corrosion of the copper. Evaluation of adsorption activity of molecule syringaldehyde according to indexes of reactivity and the study of the surface morphology of samples enable us to assume that the effectiveness of syringaldehyde at final stage is due to chemisorption of volatile organic components, which then interact and are transformed into the surface phase film that contains copper ions (corrosion products).

4. Conclusions

The syringaldehyde was found to be an effective inhibitor the copper in simulated atmospheric water. The inhibition efficiency was found to increase with time during the 48 hour of pre-treatment performed in this study, and reached ~ 98% for the largest considered inhibitor concentration. The presence of protective film considerably reduces the corrosion attacks through the formation of a protective layer which acts as a physical barrier against aggressive ions. Polarization curves indicated that syringaldehyde acted essentially as mixed type inhibitor, it suppresses both anodic and cathodic reactions for copper in simulated atmospheric water, retarding the dissolution of copper by blocking of metal surface. The results of EIS measurements indicated that the corrosion of steel is mainly controlled by the diffusion process. The morphology study elucidated the development of film on the specimen immersed in vapor phase of syringaldehyde. The inhibition of syringaldehyde is attributed to its interaction with surface of cooper and formed a chemisorption thin protective film. Quantum structure-activity relationships have been used to study the effect of molecular structure on inhibition efficiency of the syringaldehyde. High value of E HOMO is likely to indicate a tendency of the inhibitor to donate electrons to appropriate acceptor molecule, Cu surface, of low empty molecular orbital energy. Quantum-chemical calculations confirm that the syringaldehyde can be adsorbed both by electrostatic potential, forming a physically adsorbed layer and blocking the surface due to chemically adsorbed molecules.

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