A correlation between *Malva sylvestris* extracts molecules and their corrosion inhibition capabilities

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Experimental and quantum chemical investigations have been coupled in order to determine anticorrosion potential of *Malva sylvestris* extract molecules. The plant extract is a mixture of chemicals of which only four are abundant. Two groups of molecules are evidenced using quantum chemical parameters. The electrochemical investigation has classified the plant extract as a mixed-type inhibitor. The %EI has been only 54.5% due to antagonistic effects of the extract molecules.

Keywords: corrosion, green inhibitor, Malva sylvestris.

УДК 620.197

INTRODUCTION

Hazardous effects of some synthetic corrosion inhibitors have motivated scientists to use products of natural origin for materials preservation. Since the review paper of Raja et al. [1], many plants extracts have been tested as corrosion inhibitors. However, there is scared literature dealing with quantitative and/or qualitative relationships between inhibition efficiency and their molecular reactivity.

The present work is an attempt to correlate some molecule structures of the *Malva sylvestris* extracts with their corrosion inhibition capabilities. Experimental and quantum chemistry computations techniques are coupled in order to achieve this purpose.

EXPERIMENTAL

10 μl of the *Malva sylvestris* extract were analyzed by gaz chromatography coupled with a mass spectrometry detector (GC/MS) using Hewlett Packard-GCD-1800A model equipped with an electron impact ionization mass spectrometer and a HP-5 capillary fused silica column (30 m, 0.25 mm i.d., 0.25 nm film thickness). The oven temperature was held at 100°C programmed at 10°C/min to 250°C. Other operating conditions were as follows: carrier gas He (99.99%); injector temperature 250°C; detector temperature 280°C; split ratio 1:25.

Quantum calculations were performed using the Gaussian (version 03) program. Exchange and correlation calculations were investigated with the functional hybrid DFT B3LYP and the 6-31++G(d,p) orbital basis sets for all atoms.

A classical three-electrode cell was used for the electrochemical characterizations with a saturated calomel electrode as a reference electrode and the platinum wire as a counter one. The electrochemical set-up consisted of an AutoLab PGSTAT 30 potentiostat. Software GPES was used for instrumentation control and data treatment.

RESULTS AND DISCUSSION

Extraction – identification of green inhibitors from Malva sylvestris

The *Malva sylvestris* extracts were obtained when 6g of the plant leaves were left in 125 mL of methanol at room temperature. After one hour, a greenish solution was isolated. It was analyzed without further treatments by GC/MS. The chromatogram obtained is displayed in Fig. 1.

A huge number of peaks were detected. Their retention times varied between 10 and 50 minutes (Table 1).

The extract was concluded to be a mixture containing a great number of molecules. However, only four peaks were identified as the most abundant. The corresponding compounds are summarized in Table 1.

Quantum investigation

The optimized structures of the four investigated compounds obtained at B3LYP 6-31++G(d,p) level of computations are shown in Fig. 2.

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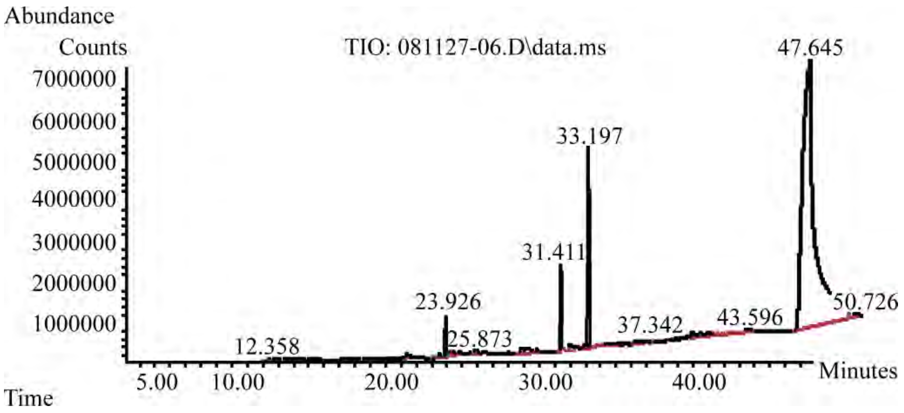
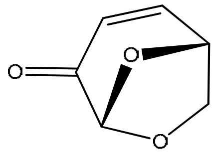
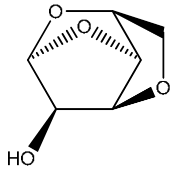
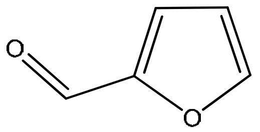
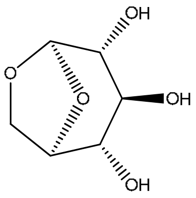
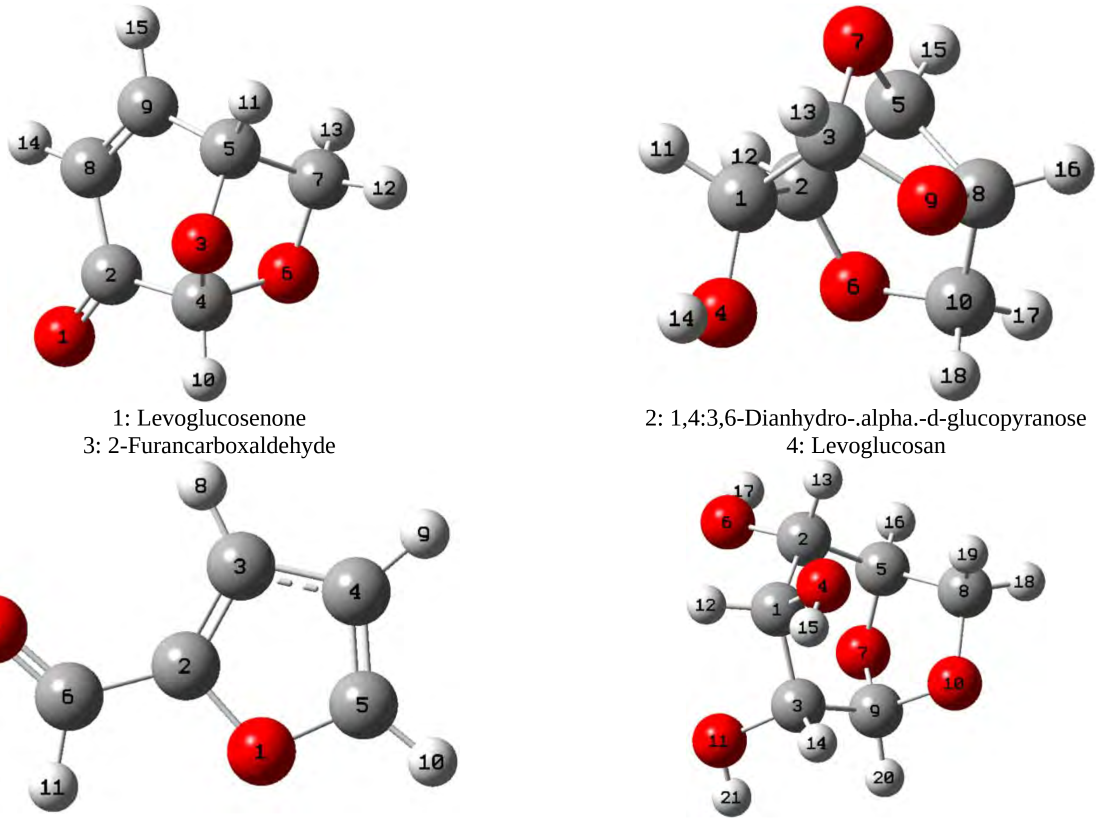


Fig. 1. GC/MS analysis of *Malva sylvestris* extract.

Table 1. Characterization of the most abundant chromatographic peaks of *Malva sylvestris* extract

Peak	1	2	3	4
Retention Time (mn)	23.926	31.411	33.197	47.645
Name	Levoglucosenone (LEONE)	1,4:3,6-Dianhydro-alpha.-d-glucopyranose (DGOSE)	2-Furancar-boxaldehyde (FHYDE)	Levoglucosan (LESAN)
Formula	$C_6H_6O_3$	$C_6H_8O_4$	$C_6H_6O_3$	$C_6H_{10}O_5$
2D Structure				

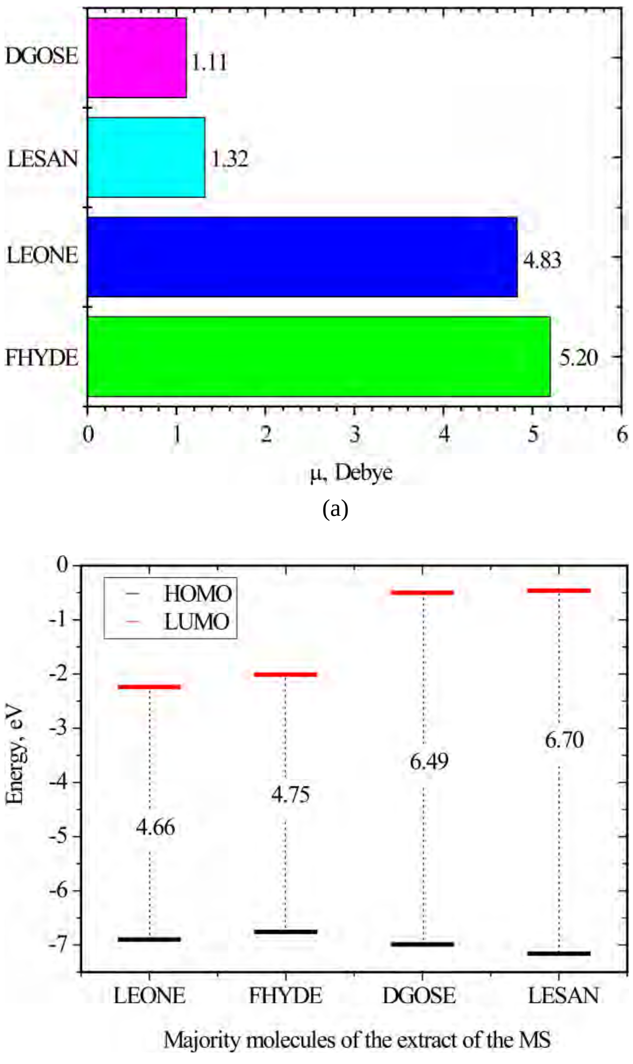


1: Levoglucosenone
3: 2-Furancarboxaldehyde

2: 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose
4: Levoglucosan

Fig. 2. Optimal space distributions of the extract majority molecules – 1: Levoglucosenone; 2: 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose; 3: 2-Furancarboxaldehyde; 4: Levoglucosan.

Quantum chemical parameters μ (dipole moment), ε_{HOMO} (the highest occupied molecular orbital energy), ε_{LUMO} (the lowest unoccupied molecular orbital energy) and the gap energy $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) are presented in Fig. 3.



(a)

(b)

Fig. 3. μ, ε_{HOMO}, ε_{LUMO}, $\Delta\varepsilon$ for the majoritary molecules of *Malva sylvestris*.

A ranking for the dipole moment established was: DGOSE < LESAN < LEONE < FHYDE (Fig. 3a). Although, in literature there is no agreed view concerning the correlation between the dipole moment and the inhibition effectiveness [2]; low values of dipole moment favour inhibitor molecules accumulation on the surface thus increasing the inhibition effectiveness [3]. However, some other researchers suggest the opposite correlation where high dipole moment enhances the adsorption on the metal surface which, in turn, contributes to higher inhibition effectiveness [4, 5].

Fig. 3b reveals that FHYDE has the highest HOMO energy and LEONE has the lowest LUMO energy. Indeed, they have the lowest values of $\Delta\varepsilon$: 4.75 eV and 4.66 eV, respectively. It is established [6] that the higher HOMO energy of an inhibitor, the greater is the tendency of offering electrons to unoccupied orbitals of metals. Furthermore, a lower LUMO energy is related to electrons acceptance from metal surfaces [6]. The gap energy is an important parameter for the reactivity of the inhibitor towards the adsorption on metallic surface. The reactivity of the molecule increases as $\Delta\varepsilon$ decreases leading to enhancement of the corrosion inhibition efficiency [6].

Some HSAB (Hard and Soft Acids and Bases) parameters such as electronegativity (χ), chemical hardness (η) as well as electrophilicity index (ω) were recently defined [7, 8] as:

$$\chi \approx -\frac{1}{2}\left(\varepsilon_{HOMO} + \varepsilon_{LUMO}\right), \tag{1}$$

$$\eta \approx \frac{1}{2}\left(\varepsilon_{LUMO} - \varepsilon_{HOMO}\right), \tag{2}$$

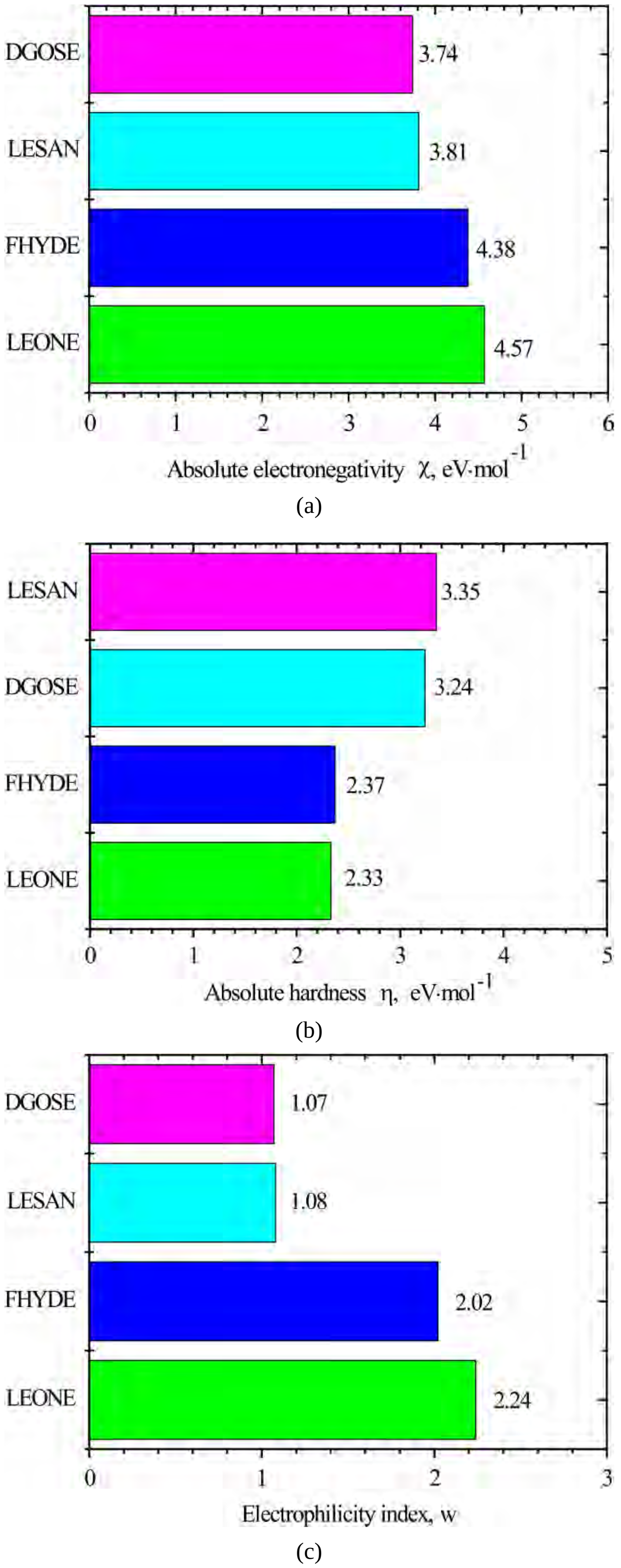
$$\omega = \frac{1}{4}\frac{\chi_{mol}^{2}}{\eta_{mol}}. \tag{3}$$

The calculated values for the three parameters are given in Fig. 4.

The data in Fig. 4a show that electronegativity varies between 3.7eV.mol^{-1} and 4.6 eV.mol^{-1}, where LEONE > FHYDE > LESAN > DGOSE. If a metal and an inhibitor are brought together, the flow of electrons will generally occur from the molecule of lower electronegativity to the metal that has higher electronegativity until the values of the chemical potential become equal [9].

From Fig. 4b one can conclude that LEONE admitted the lowest η value. Chemical hardness is used to measure the molecular stability and reactivity. A hard molecule has a large gap energy and a soft molecule has a small one. Soft molecules are generally more reactive because they could easily offer electrons to an acceptor [10]. In a corrosion system, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid. Bulk metals are often considered as soft acids and thus soft molecules are most effective for corrosion inhibition [10]. It is also assumed that hard acids reacted preferentially with hard bases [8]. Hence, some corrosion inhibitors capabilities could be also identified for such chemicals.

The electrophilicity index, which shows the ability of the inhibitor molecules to accept electrons [11], follows the trend: DGOSE < LESAN < FHYDE < LEONE. Thus, LEONE exhibits the highest value of electrophilicity (Fig. 4c), which confirms its high capacity to accept electrons. Thus, inhibitor molecule electrons can use unoccupied d orbitals of metals to form coordinate bonds. The inhibitor molecule can also accept electrons with its anti-bonding orbitals to form back-donating bond.



(a)

(b)

(c)

Fig. 4. χ, η and ω evolution for the majoritary molecules of *Malva sylvestris*.

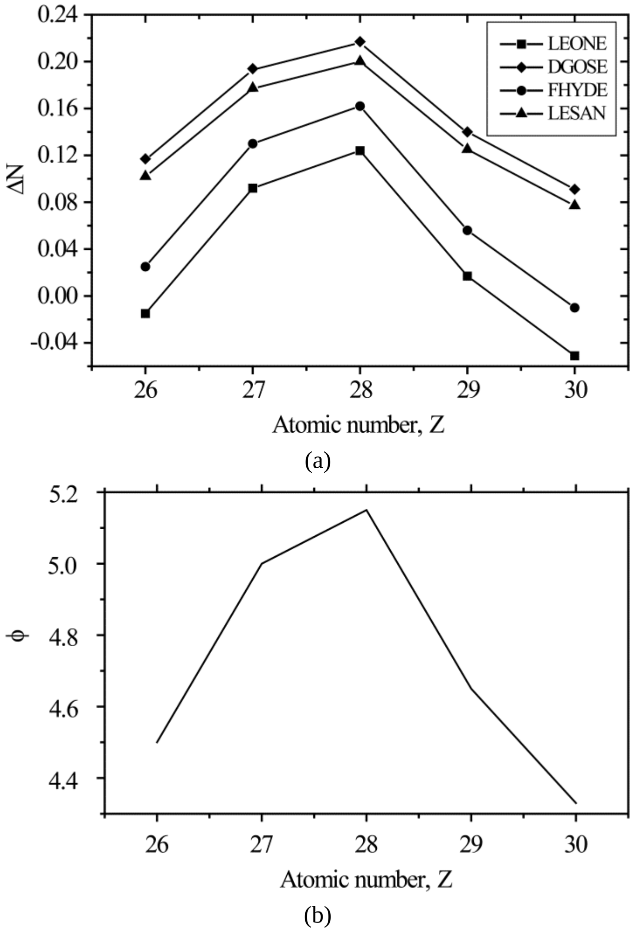
These donation and back-donation processes strengthen the adsorption phenomena [11].

In order to tentatively evaluate the interaction of the *Malva sylvestris* extract molecules with some metal surfaces ($_{26}$Fe, $_{27}$Co, $_{28}$Ni, $_{29}$Cu and $_{30}$Zn), the number of electrons transferred (ΔN) was calculated using the following equation [5, 7, 8]:

$$\Delta N = \frac{\chi_{metal} - \chi_{mol}}{2\left(\eta_{metal} + \eta_{mol}\right)} = \frac{\Phi - \chi_{mol}}{2\eta_{mol}} \qquad (4)$$

where: χ_{metal} is metal electronegativity; χ_{mol} – molecule electronegativity; Φ – work-function; η_{metal} – metal chemical hardness; η_{mol} – molecule chemical hardness.

The choice of those five metals is based on the complex relationship between the work function Φ and the atomic number Z in the intervals occupied by transition metals [12]. For the metal surface, the work-function Φ is taken as its electronegativity, whereas the chemical hardness is neglected, being an exceedingly small number, because η of bulk metals is related to the inverse of their density of states at the Fermi level [13]. Calculated values for ΔN are given in Fig. 5.



(a)

(b)

Fig. 5. Fraction of electrons transferred ΔN (a) and work function Φ (b) evolutions for the majoritary molecules of *Malva sylvestris* for five metals considered.

ΔN showed the same behaviour independently on the metal considered. In fact, it increased reaching a maximum at $_{28}$Ni (Fig. 5a). Then, the curve slope became negative and the fraction of electrons transferred decreased. Such behaviour is close to that exhibited by the work function Φ in the same Z domain (Fig. 5b). Among the majoritary molecules of the extract, DGOSE showed the most important

ΔN. This could be attributed to its low electronegativity. Negative values for ΔN were observed for LESAN, with $_{26}$Fe and $_{30}$Zn, as well as for LEONE, with the latter. In contact with these metals, both molecules were confirmed to receive electrons.

Polarization measurements

Electrochemical tests were carried out on XC48 mild steel to confirm the corrosion inhibition capabilities of *Malva sylvestris.* Polarization curves were plotted for the material simulating $_{26}$Fe in 0.5M NaCl with and without addition of the plant extract (Fig. 6).

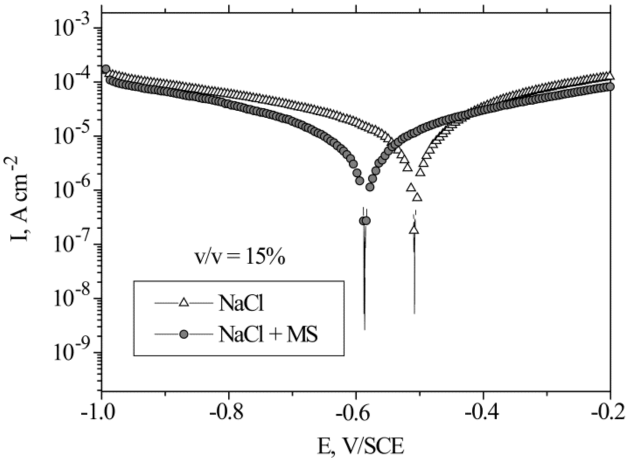


Fig. 6. Polarization curves of XC48 mild steel immersed at 30°C in NaCl 0.5 mol L^{-1} without and with addition of *Malva sylvestris* extract at 15% (v/v). Polarization from -1V to -0.2V at a fixed scan rate of 0.1 mV s^{-1}.

Four sections were evidenced on the polarization curves. The first one ranges from -1000 mV/SCE to -800 mV/SCE corresponding to the cathodic region. It reflects the over potential domain where water reduction reaction takes place. The second section ([-800; -650 mV/SCE]) is a potential window of film formation, leading to a pseudo limiting current density. An apparent Tafel behaviour was detected in the third section. It corresponds to the potential region out of which mixed charge transfer and mass transport controlling kinetics are usually assumed. For the fourth section, the current density increased due to the formation of Fe(II) species:

$$\mathrm{Fe} \rightarrow \mathrm{Fe(II)} + 2e^{-}. \tag{5}$$

In the Tafel domain, extrapolation of linear line to corrosion potential gives a straight line and the slope gives both β_a and β_c, and the intercept gives the corrosion current. The Ecorr and Icorr values have been calculated using the Tafel extrapolation method (Table 2).

It was observed that Ecorr shifted to negative values when the plant extract added. The anodic slope β_a was about 90 mV^{-1} for the blank. It decreased when the *Malva sylvestris* extract introduced reached 74 mV^{-1}. It was also noticed that adding the plant extract affected the cathodic slope. In fact, it was equal to -0.172 mV^{-1} for the blank. It moved towards -89 mV^{-1} for the interface material/chloride/plant extract. The corrosion current Icorr was 2.6 μA cm^{-2} for the material/chloride interface. It was divided by factor 2 when the *Malva sylvestris* extract was added. The proportionality factor *B* was about 87.3 mV for the blank system. It was multiplied by a factor 2 for the system material/chloride electrolyte/*Malva sylvestris* extract, reaching 195.1 mV.

Table 2. Electrochemical parameters for mild steel without and with addition of *Malva sylvestris* (MS) extract

	$-E_{corr}$ (mV/SCE)	β_a (mV^{-1})	$-\beta_c$ (mV^{-1})	I_{corr} (μA cm^{-2})	*B* (mV)	%IE
NaCl	508	92.6	171.9	2.63	87.3	–
NaCl + MS	586	74.2	88.9	1.20	195.1	54.4

The electrochemical investigation confirmed the corrosion inhibition capabilities of the *Malva sylvestris* molecules as both Tafel slopes β_a and β_c decreased when the plant extract was added. Hence, it was classified as a mixed-type inhibitor. We also modelled the percentage of inhibition efficiency %EI, which was calculated in [14] as follows:

$$\%EI = 100 \cdot \frac{I_{corr}(T) - I_{corr}(T + MS)}{I_{corr}(T)} \tag{6}$$

where I_{corr} (*T*) is the corrosion current of the blank and Icorr (*T* + *MS*) is the corrosion current of the blank with the *Malva sylvestris* extract.

The inhibition efficiency percentage was only 54.5%. Such result could be attributed to the antagonistic effects of various extract molecules. In fact, low electronegativity owns offered electrons to the surface whereas hard chemicals tended to receive electrons from the metal (corrosion reaction) forming back-donation bond.

CONCLUSIONS

The present research was undertaken in order to tentatively establish a correlation between the *Malva sylvestris* extract molecules and their corrosion inhibition capabilities. GC/MS analysis of an alcoholic plant extract gave rise to a mixture containing a huge number of chemicals, but only four of them were the most abundant. Some of their quantum chemical parameters, such as dipole moment (μ), the highest occupied molecular orbital energy (ε_{HOMO}), the lowest unoccupied molecular orbital energy (ε_{LUMO}), the gap energy ($\Delta\varepsilon$) electronegativity (χ), chemical hardness (η) and electrophilicity index (ω) were evaluated at the

B3LYP 6-31++$G(d,p)$ level. Two groups of molecules were evidenced. The first admitted the lowest μ, ε_{HOMO}, χ, ω and the highest ε_{LUMO}, Δε and η. They were predicted to offer electrons to metal surfaces until the values of their chemical potential becoming equals. The second chemical group presented the opposite quantum chemical characteristics (highest μ, ε_{HOMO}, χ, ω and lowest ε_{LUMO}, Δε and η). Such chemicals were concluded to receive electrons from metals forming back-donation bond.

The fraction of electrons transferred was also evaluated for five transition metals: ${}_{26}$Fe, ${}_{27}$Co, ${}_{28}$Ni, ${}_{29}$Cu and ${}_{30}$Zn. It was noticed that ΔN exhibited a similar behaviour as the work function Φ in the same Z domain. Among the molecules of the extract, DGOSE showed the most important ΔN as it presented the lowest electronegativity. LESAN, with ${}_{26}$Fe and ${}_{30}$Zn, and LEONE, with the last metal, delivered negative values for ΔN, and hence, receiveed electrons from their surfaces.

The electrochemical investigation confirmed the corrosion inhibition capabilities of the *Malva sylvestris* molecules as both Tafel slopes β_a and β_c decreased when the plant extract was added. Hence, it could be classified as a mixed-type inhibitor. However, the inhibition efficiency percentage was only 54.5%. Such result could be attributed to the antagonistic effects of various extract molecules.

REFERENCES

1. Raja P.B., Sethuraman M.G. Natural Products as Corrosion Inhibitor for Metals in Corrosive Media. A Review. *Materials Letters*. 2008, **62**(1), 113–116.
2. Obot I.B., Obi-Egbedi N.O. Theoretical Study of Benzimidazole and its Derivatives and their Potential Activity as Corrosion Inhibitors. *Corrosion Science*. 2010, **52**(2), 657–660.
3. Khalil N. Quantum Chemical Approach of Corrosion Inhibition. *Electrochimica Acta*. 2003, **48**(18), 2635–2640.
4. Sahin M., Gece G., Karc F., Bilgiç S. Experimental and Theoretical Study of the Effect of Some Heterocyclic Compounds on the Corrosion of Low Carbon Steel in 3.5% NaCl Medium. *Journal of Applied Electrochemistry*. 2008, **38**(6), 809–815.
5. Kokalj A. Is the Analysis of Molecular Electronic Structure of Corrosion Inhibitors Sufficient to Predict the Trend of their Inhibition Performance. *Electrochimica Acta*. 2010, **56**(2), 745–755.
6. Rahim A.A., Rocca E., Steinmetz J., Kassim M.J. Inhibitive Action of Mangrove Tannins and Phosphoric Acid on Pre-rusted Steel Via Electrochemical Methods. *Corrosion Science*. 2008, **50**(6), 1546–1550.
7. Parr R.G., Pearson R.G. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *Journal of the American Chemical Society*. 1983, **105**(26), 7512–7516.
8. Pearson, R.G. Absolute Electronegativity and Hardness: Application to Inorganic Chemistry. *Inorganic Chemistry*. 1988, **27**(4), 734–740.
9. Martinez S., Stagljar I. Correlation between the Molecular Structure and the Corrosion Inhibition Efficiency of Chestnut Tannin in Acidic Solutions. *Journal of Molecular Structure (Theochem)*. 2003, **640**(1–3), 167–174.
10. Obi-Egbedi N.O., Obot I.B., El-Khaiary M.I., Umoren S.A., Ebenso E.E. Computational Simulation and Statistical Analysis on the Relationship between Corrosion Inhibition Efficiency and Molecular Structure of Some Phenanthroline Derivatives on Mild Steel Surface. *International Journal of Electrochemical Science*. 2011, **6**, 5649–5675.
11. Obi-Egbedi N.O., Obot I.B., El-Khaiary M.I. Quantum Chemical Investigation and Statistical Analysis of the Relationship between Corrosion Inhibition Efficiency and Molecular Structure of Xanthene and its Derivatives on Mild Steel in Sulphuric Acid. *Journal of Molecular Structure*. 2011, **1002**(1–3), 86–96.
12. Michaelson, H.B. The Work Function of the Elements and its Periodicity. *Journal of Applied Physics*. 1977, **48**(11), 4729–4733.
13. Yang W., Parr R.G. Hardness, Softness and the Fukui Function in the Electronic theory of Metals and Catalysis. *Proceedings of the National Academy of Sciences of the United States of America*. 1985, **82**, 6723–6726.
14. Gopiraman M., Sakunthala P., Kesavan D., Alexramani V., Kim I.S., Sulochana N. An Investigation of Mild Carbon Steel Corrosion Inhibition in Hydrochloric Acid Medium by Environment Friendly Green Inhibitors. *Journal of Coatings Technology Research*. 2012, **9**(1), 15–26.

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Реферат

Экспериментальные и квантово-химические исследования были проведены для установления взаимосвязи между молекулами экстракта *Malva sylvestris* и их антикоррозийными свойствами. Экстракт растения представлял собой смесь химических реагентов, из которых только 4 были избыточными. Две группы молекул были определены путем использования квантово-химических параметров. С помощью электрохимических исследований растительный экстракт был классифицирован как ингибитор смешанного типа. Процент ингибирования составил всего лишь 54,5 %, вследствие антагонистического эффекта молекул экстракта.

Ключевые слова: коррозия, зеленый ингибитор, Malva sylvestris.