

VALERIAN EXTRACT USED AS POTENTIAL CORROSION INHIBITOR FOR CARBON STEEL IN DIFFERENT MEDIA

George-Daniel DIMA^a, Oana-Tabita ȘERBOIU^a,
Mircea Laurențiu DAN^{a,*}, Liviu-Virgil COSTEA^a

ABSTRACT. The paper investigates the corrosion inhibition property of the Valerian (*Valeriana officinalis*) extract for carbon steel in acid and neutral solutions. The extracted natural compounds from plants have been reported in the literature as efficient corrosion inhibitors due to their stability to different environments, eco-friendly character, and their low cost. The usefulness of a different type of valerian species, in corrosion protection, by inhibiting the anodic oxidation reaction due to the improvement of the development of a passivating film, has been reported earlier for the *Valeriana wallichii* root extract in the corrosion of mild steel in different acidic media. Based on the latter findings, our studies have been performed in three different media, H₂SO₄, HCl and NaCl. An array of electrochemical techniques such as Tafel polarization, cyclic voltammetry, as well as chronopotentiometry have been employed to elucidate the corrosion behavior of carbon steel within the investigated media, containing various amounts of *Valeriana officinalis* extract. Quantum chemical calculations have been employed in order to assess the adsorption capacity of the mentioned extract onto the metal surface. The latter extract exhibits inhibitory effects in the studied media, even at small concentrations.

Keywords: *natural extracts; green corrosion inhibitor; Tafel linear polarization; molecular modelling, sustainability*

^a University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Laboratory of Electrochemistry, Corrosion and Electrochemical Engineering, 6 Pârvan, 300223 Timisoara, Romania

* Corresponding author: mircea.dan@upt.ro



INTRODUCTION

Corrosion is the deterioration of the metallic material due to the action of a corrosive environment. This causes problems of an economic nature and, from the consumer safety point of view, the destabilizing of the component materials, the durability over time of certain metallic tools and goods being seriously affected [1]. In recent times, new environmental friendly anti-corrosion protection methods have been developed based on the use of substances that adsorb themselves onto the metal surface, either physically by weak interactions, or chemically by covalent coordinative bonds between the empty orbitals of the metal and the non-participating electron pairs at the level of the heteroatoms of the component groups of the inhibitors [2].

Corrosion of steel used in the field of construction, namely that of the manufacture of fittings represents a major issue. Elements such as resistance structures of buildings or road infrastructure that interact with the sea water such as bridge piers, underwater tunnels involve huge secondary costs if a good anti-corrosion protection plan is not designed and implemented in advance [3]. One may mention examples of organic compounds that prevent mild steel from corroding in a neutral environment include some macrocyclic compounds that contain nitrogen, sulfur, and oxygen heteroatoms such as compounds with porphyrinic rings - porphyrin tetra benzoic acids and porphyrin-F-Pd [4]. In an acidic environment, heterocyclic compounds derived from the pharmaceutical field which are predominantly employed are Amoxicillin and Penicillin G [5], Cefazolin [6], diethylcarbamazine [7], active compounds from expired drugs such as Tobramycin [8], Atorvastatin [9], Nifedipine [10], amino acids containing a ring with a nitrogen heteroatom such as L-tryptophan, and its Schiff base [11, 12], respectively L-proline [13]. Recently, due to their natural availability and the relatively simple production methods, implying only a few steps of extraction and purification, starting from the raw plant, recent research has been aimed on corrosion inhibitors containing extracts from different plant components (root, stem, leaves, fruit or bark), due to their high solubility in different environments, especially in acidic ones. Each natural extract consists of a multitude of organic compounds such as amino acids, bioflavonoids, unsaturated fatty acids, which mostly have electron donor groups. Their inhibitory efficiency approaches that of many potentially toxic, synthetic organic inhibitors [14]. One of the main disadvantages regarding inhibitors based on plant extracts resides in their short shelf life. Over time and if stored in improper conditions they could be degraded by microorganisms and fungi, thus considerably reducing their inhibition efficiency [2]. The most common examples of green inhibitors for mild steel comprise extracts of *Nicotiana tabacum* in a corrosive environment of H_2SO_4 [15], the papaya

seeds extract in HCl [16], and lemon balm extract in HCl [17], respectively that of stem of pineapple extract as a mixed inhibitor for carbon steels in hydrochloric acid environment [18]. In all mentioned cases, the adsorption of substances from the extract to the metal is both physical and chemical. The main reason for the use of natural extracts as a corrosion inhibitor is the ease of patenting the method at the expense of other types of synthetic compounds, in relation to the impact on the environment or the increase in the resistance of some microorganisms in the case of use, for example of medicines. In the literature, the inhibitory properties of *Valeriana willichii* root extracts (Indian valerian) are reported [19], our research being oriented towards extracts from herbaceous plants from the Valerianaceae family, namely *Valeriana officinalis*.

RESULTS AND DISCUSSION

Cyclic voltammetry

To gather initial information about the resistance to electrochemical oxidation/reduction of valerian tincture, as well as how the compounds present in the tincture influence the anodic and cathodic processes, a series of cyclic voltammetry tests were conducted. Figures 1a, b, and c show the results of cyclic voltammetry performed in the test solutions. The results in figure 1a, recorded in a sulfuric acid solution without valerian tincture, show typical peaks for a voltammogram in a strongly acidic environment. When the potential values become more negative than 0 V vs. $E_{Ag/AgCl}$ the cathodic process of reducing H^+ ions from the acid is observed, followed by an anodic peak indicating the oxidation of hydrogen on the platinum electrode surface. A very low intensity current level is observed in the potential range of + 0.5 V vs. $E_{Ag/AgCl}$ and + 1.50 V vs. $E_{Ag/AgCl}$, which is related to the development of the working electrode's surface's superficial layer of platinum oxides. A distinct cathodic peak can be seen around a potential value of -0.30 V vs. $E_{Ag/AgCl}$, which corresponds to the reduction process of the oxide layer's surface during its oxidation stage. Only the process of oxygen release in an acidic environment is documented at electrode potential values more positive than +0.40 V vs. $E_{Ag/AgCl}$ on cyclic curves. A modest current level of low intensity associated with the reduction of atomic oxygen or gaseous oxygen on the surface of the metal electrode can be recognized while scanning in the reverse direction of the potential range towards the starting point, the OCP value. The anodic process of oxygen formation and release on the platinum surface is inhibited by the addition of valerian tincture in the acid medium at

two concentrations, 2.5 mL L⁻¹ and the highest concentration used in the experimental studies, 10 mL L⁻¹. This effect is seen by shifting the potentials associated with this process towards more positive values, while the cathodic processes corresponding to the reduction of H⁺ ions and the release of hydrogen are unaffected. The pronounced anodic peak is recorded on the anodic branch at a potential value of approximately +1.75 V vs. E_{Ag/AgCl} associated with the oxidation of chloride ions to atomic chlorine and their dimerization to chlorine gas on the surface of the platinum electrode on the cyclic curves in figure 1b drawn in the 0.5 M HCl solutions without and with the two additions of valerian tincture.

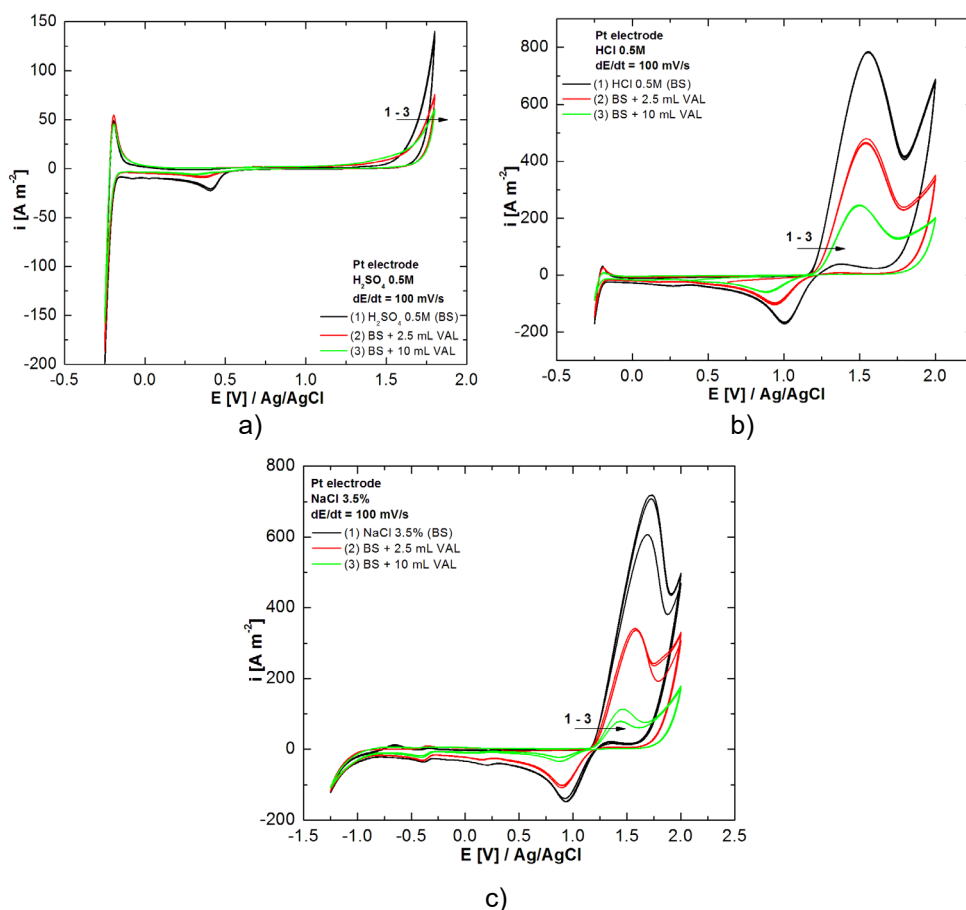


Figure 1. Cyclic voltammograms recorded on a platinum electrode in H₂SO₄ solution (a) HCl 0.5M (b) and NaCl 3.5% (c) in the absence and presence of different concentrations of valerian tincture, at a scan rate of 100 mV s⁻¹.

Because the value of the overpotential associated with the oxidation of chloride on the platinum electrode is lower than that associated with the competing process - the release of oxygen - this oxidation process occurs at potentials more negative than those corresponding to the oxidation of O^{2-} ions with the formation of atomic oxygen and then gaseous oxygen. Similar to those observed in the hydrochloric acid solutions are the cyclic voltammograms in figure 1c displayed in the 3.5% NaCl saline solutions without and with the two inhibitor concentrations of valerian tincture (2.5 and 10 mL L⁻¹). The cathodic peak at potential value -0.50 V vs. $E_{Ag/AgCl}$ which corresponds to the global initial stage in the conversion of H^+ ions to hydrogen atoms adsorbed on the platinum surface, is notable. Valerian tincture and its components are electrochemically stable over the entire potential range in which they were traced, according to the cyclic voltammetry data collected on the platinum electrode in the three corrosive environments. This means that they do not undergo electrochemical transformations (oxidation and reduction processes).

Chronopotentiometry studies – Open circuit potential determination

Figure 2 depicts the change in equilibrium potential for the working electrode in H_2SO_4 and HCl solutions of 0.5 M and 1 M, respectively. We can conclude that after 1 h, during which the electrode potential values were recorded, the electrochemical system had reached a quasi-stationary state, a state sufficient for initiating corrosion studies using the linear polarization method.

Table 1. Determination of E_{OCP} in solutions of H_2SO_4 0.5 M, HCl 0.5 M, respectively NaCl 3.5%

Electrode	$V_{Tincture}$ [mL L ⁻¹]	T [°C]	E_{OCP} [mV]/Ag/AgCl		
			H_2SO_4 0.5 M	HCl 0.5 M	NaCl 3.5%
S355J2	0	25°C	-432	-435	-655
	1		-430	-429	-645
	2.5		-421	-427	-638
	5		-417	-422	-632
	10		-414	-418	-626

As a function of the valerian tincture concentration added to the corrosive medium, Table 1 shows the values of equilibrium potentials (open circuit potentials, or E_{OCP}) of the working electrode in the three electrolytes used as aggressive media.

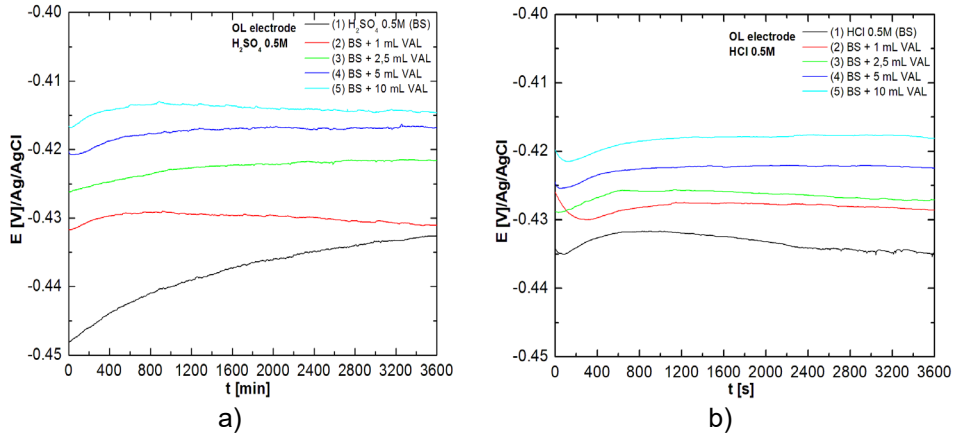


Figure 2. Evolution during 1 h of the equilibrium potential of the S355J2 type carbon steel electrode in solution in solution of H₂SO₄ 0.5 M (a) HCl 0.5 M (b) with different inhibitor concentrations

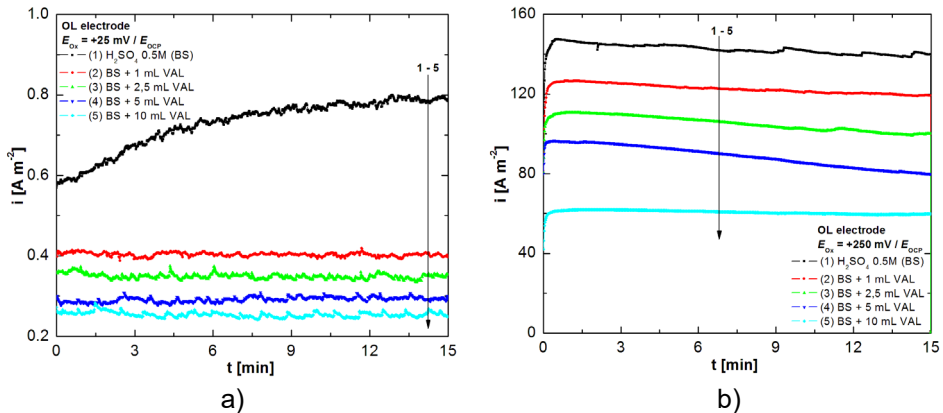


Figure 3. Chronoamperograms in H₂SO₄ 0.5 M for E_{Ox} = +25mV/E_{corr} (a), respectively for E_{Ox} = +250 mV/E_{corr} (b).

Table 2. Oxidation current density values recorded for 15 minutes in chronoamperometric determinations in H₂SO₄ 0.5 M

Electrode	Test solution	E _{Oxidation}	
		+25 mV / E _{OCP}	+250 mV / E _{OCP}
		i _{Oxidation} [A m ⁻²]	
S355J2	H ₂ SO ₄ 0.5 M (SB)	0.79	139
	SB + 1 mL L ⁻¹ VAL	0.40	120
	SB + 2.5 mL L ⁻¹ VAL	0.35	100
	SB + 5 mL L ⁻¹ VAL	0.29	79
	SB + 10 mL L ⁻¹ VAL	0.25	60

The E_{OCP} values in all three aggressive environments move towards slightly more positive values when the valerian tincture is added to the electrolyte, as the inhibitor concentration increases, as compared to the recorded carbon steel electrode potential value in solutions without valerian tincture. This variation of the E_{OCP} indicates that on the surface of the tested electrode made of carbon steel, organic molecules from the valerian tincture are adsorbed on the active sites, which form a protective layer that functions as a barrier against corrosion.

Chronoamperometry studies

Introduced as a method to study the corrosion processes of metals and alloys recently, from the perspective of the effectiveness of the use of corrosion inhibitors added in laboratory studies in various aggressive environments, the chronoamperometric method is based on the analysis of the time variation of the current under the conditions in which the electrode potential is kept at a constant value.

From the diagrams shown in Figure 3 a and b, the current density values corresponding to the oxidation of S355J2 type carbon steel samples in H_2SO_4 0.5 M solutions are shown in Table 2.

By examining the chronoamperometric data shown in the table above, one can see that as the amount of valerian tincture added to the H_2SO_4 0.5 M solutions increases, the values of the current densities corresponding to the oxidation of the S355J2 type carbon steel samples decrease. This decrease in current densities reflects a reduction in the values of corrosion rates as a result of the increased degree of adsorption of the tincture's inhibitory components on.

Corrosion studies by the linear polarization method

The three diagrams were recorded after nitrogen bubbling to remove oxygen from the test solution. In the event when the test electrolyte contains physically dissolved oxygen, this was done to avoid any possible side reactions that might occur at the electrode or on it.

Additionally, it was carried out after the electrode and the electrolyte solution had attained a particular equilibrium state.

In Figures 4a and b are showed the Tafel plots recorded on S355J2 carbon steel samples in the absence and presence of different valerian tincture concentrations added in the three corrosive environments.

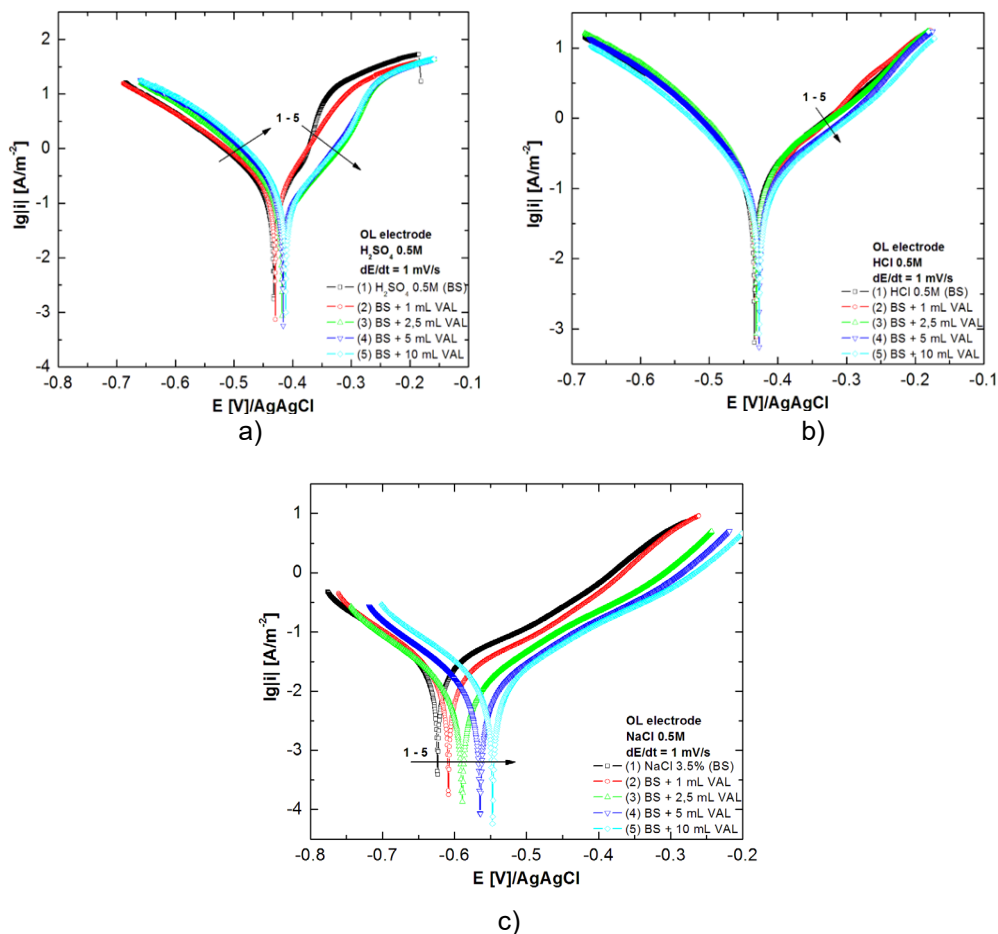


Figure 4. Tafel polarization curves recorded, at 25°C, on S355J2 type carbon steel electrode in 0.5M H₂SO₄ (a), 0.5M HCl (b) and 0.5M NaCl (c) solutions in the absence/presence different valerian tincture concentrations.

The fitting of the linear polarization curves recorded for each determination, in order to calculate the parameters specific to the corrosion processes of the S355J2 type carbon steel samples are presented in Table 3.

Table 3. Electrochemical parameters determined by the Tafel method on S355J2 type carbon steel electrode in 0.5 M H₂SO₄, 0.5 M HCl and 3.5% NaCl solutions without and with the addition of valerian tincture, at 25°C.

Corrosion media	V _{Tincture} [mL]	<i>i</i> _{corr} [μA cm ⁻²]	<i>E</i> _{corr} [mV]	- <i>b</i> _c [mV dec ⁻¹]	<i>b</i> _a [mV dec ⁻¹]	<i>R</i> _p [Ω cm ²]	<i>v</i> _{corr} [mm y ⁻¹]	<i>IE</i> [%]	θ
H₂SO₄ 0.5 M	0	126.1	-432	118	73	155	3.62	-	-
	1	91.9	-429	98	64	183	2.14	27.12	0.27
	2.5	54.3	-422	73	60	263	1.46	56.94	0.57
	5	45.3	-418	56	55	266	1.06	64.08	0.64
	10	20.7	-412	44	49	486	0.97	83.58	0.84
HCl 0.5 M	0	128.7	-434	107	125	195	3.7	-	-
	1	93.8	-431	101	120	254	2.41	27.12	0.27
	2.5	59.3	-430	97	115	385	2.11	53.92	0.54
	5	40.4	-427	93	108	537	1.62	68.61	0.69
	10	22.5	-424	89	103	921	1.12	82.52	0.83
NaCl 3.5%	0	108.2	-658	68	85	152	0.205	-	-
	1	79.7	-623	61	69	176	0.186	26.34	0.26
	2.5	53.7	-602	54	58	226	0.161	50.37	0.50
	5	35.6	-571	49	48	296	0.138	67.10	0.67
	10	19.5	-557	48	43	505	0.115	81.98	0.82

The concentration of valerian tincture in the aggressive medium and its proportionality with the volume of tincture added are the defining factors for its inhibitory efficiency in the corrosion process of carbon steel S355J2 in H₂SO₄ medium.

Similarly, to the HCl and NaCl media, a decrease of corrosion rate is observed, followed, as is normal, by an increase in inhibitory efficiencies and an increase in inhibitor concentration.

Simultaneously, variations in polarization resistance are observed, with values ranging from a few hundred to 921 Ω in the case of the maximum inhibitor concentration.

According to the results in Table 3, valerian tincture acts as a corrosion inhibitor for the carbon steel used in the experimental studies of type S355J2 in aggressive sulfuric acid environments, HCl environments, and corrosive saline environments.

Molecular modelling

The extracts obtained from the root of the *Valeriana Officinalis* plant represent mixtures containing numerous compounds, their composition varying significantly depending on the obtaining method, seasonality, but especially on the geographical area of origin of the biological material. Since recent literature data reveal that the essential oils obtained from VO cultivated in the vicinity of our country are characterized by high contents of bornyl acetate ((1,7,7-trimethyl-2-bicyclo[2.2.1]heptyl acetate)) and alpha fenchene (7,7-dimethyl-2 methylidenebicyclo[2.2.1]heptane) [22], the latter compounds have been subjected to further computational studies.

Electrochemical properties of various organic substrates are intrinsically linked to the electronic structure of their frontier orbitals, hence quantum chemical calculations of frontier orbital energies, could provide the necessary theoretical foundation to sustain the results obtained experimentally.

Quantum chemical analysis, used as a complementary technique to experimental studies, offers the possibility of elucidating the mechanisms underlying the phenomena of corrosion protection.

The energies of the frontier molecular orbitals (LUMO and HOMO respectively) as well as the energy difference (the so-called energy gap) $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ have been calculated for the B3LYP optimized structures of the mentioned compounds in vacuum.

A low value of the energy of the LUMO orbital (the lowest unoccupied molecular orbital) suggests a more pronounced tendency of the organic substrate to accept electrons, while a higher energy value of the of the HOMO orbital (the occupied molecular orbital with the highest energy level) reflect the tendency of the organic molecule to lose negative electrical charges [23].

The tendency of an organic substrate to adsorb onto the metal surface (and thus to act as a corrosion inhibitor) is all the more pronounced the lower the value of the energy difference $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$.

Data in Table 4 shows that $E_{\text{HOMO}}(\text{AF}) > E_{\text{HOMO}}(\text{BA})$, so alpha fenchene (AF) will present a more pronounced tendency to donate electrons to the metal.

The energies $E_{\text{LUMO}}(\text{BA}) < E_{\text{LUMO}}(\text{AF})$ denote that bornyl acetate (BA) has a greater ability to accept electrons from the d orbital of Fe and the value $\Delta E = 0.599$ eV related to AF reflects the increased stability of the Fe-AF complex possibly formed on the metal surface.

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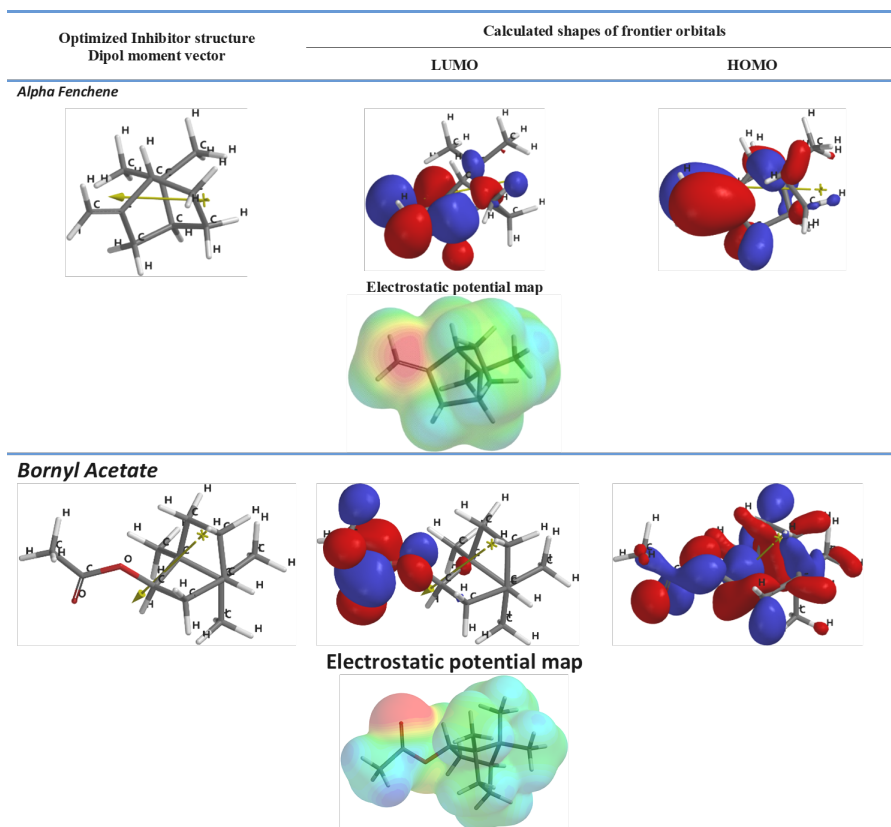


Figure 5. Frontier orbital profiles, dipole moment orientations and total charge densities mapped with electrostatic potential calculated for the optimized geometries of the two investigated main components of *Valeriana officinalis* extract

Given that the value of the ionization energy (IP) as well as that of the electron affinity (EA) can be estimated based on the energies of the frontier orbitals as per Koopmann's theorem (Eq. 1 and 2) [24, 25]:

$$E_{HOMO} = -IP \quad (1)$$

$$E_{LUMO} = -EA \quad (2)$$

we can calculate specific molecular descriptors, namely electronegativity (χ), chemical potential (μ), electrophilic index (ω). The higher the value of (χ), the lower the tendency of the substrate to give up electrons. The tendency to give up electrical charges to the base metal is more pronounced the higher the σ (molecular softness) parameter is, and respectively the lower the higher the η (molecular hardness) parameter is.

Table 4 Values of the parameters describing the global reactivity calculated for the main components of the valerian root extract

Global descriptors / eV	Substrate	
	Alpha Fenchene	Bornyl Acetate
Ionization potential (IP)	6.510	7.550
Electron affinity (EA)	0.520	0.160
Chemical potential (μ)	-3.515	-3.855
Electronegativity (χ)	3.515	3.855
Global hardness (η)	2.995	3.695
Global softness (σ)	0.167	0.135
Electrophilicity index (ω)	2.063	2.011
Electrodonating power (ω^-)	4.195	4.400
$\Delta E = E_{LUMO} - E_{HOMO}$	5.990	7.390
Dipole moment (Debye)	0.930	2.660

The dipole moment of the inhibitor molecule quantifies the degree of separation of electrical charges in that molecule. Increased values of the molecular dipole moment favor adsorption phenomena on the metal surface. The anticorrosive protection capacity increases with the increase of the dipole moment of the molecule.

Data in Table 4 reveals that the polarity of BA (2.66 D) is much more pronounced, so we can conclude that the weight of BA in the anticorrosive effect exerted by the VO extract is primary [22].

CONCLUSIONS

Studies on the corrosion of S355J2 carbon steel were conducted in three environments: strong acid solutions (0.5 M H₂SO₄, 0.5 M HCl) and saline solution (3.5% NaCl). The Tafel method and linear polarization method were used to analyze the corrosion process, and the effect of valerian tincture was studied by cyclic voltammetry on a platinum electrode in these environments.

Results showed that valerian tincture significantly impacted the anodic processes of chloride ion oxidation and O²⁻ ion oxidation in all three environments but had no notable effect on the cathodic process of H⁺ ion reduction. The adsorption of organic molecules from valerian tincture on the electrode suggests an electrostatic interaction between the tincture and the metal surface, contributing to the tincture's role as a corrosion inhibitor for S355J2 carbon steel in aggressive acid and saline environments.

EXPERIMENTAL SECTION

Materials

The corrosive media used in the experimental studies were prepared starting from pure reagent of high concentration by diluting with distilled water until the desired concentration was obtained, 0.5 M for the sulfuric acid solution, 0.5 M for the hydrochloric acid solution, respectively 3.5% for sodium chloride solution. Reactants used in the preparation stage were solutions of sulfuric acid (Merck 98%) and hydrochloric acid (Merck 37%) and sodium chloride p.a. (Merck). The corrosion inhibitor subjected to this study was valerian tincture – with a composition of 30% soft extract of valerian roots (*Valeriana officinalis*) and 70% vegetable glycerin); its inhibitory properties for the corrosion of carbon steel type S355J2 was analyzed in the three corrosive environments mentioned above.

Electrochemical methods

The electrochemical measurements were carried out in a cell with a configuration of 3 electrodes, the S355J2 steel working electrode, two graphite bars as counter electrodes and an Ag/AgCl reference electrode. The experimental determinations were recorded using the software of the BioLogics SP150N potentiostat/galvanostat, by acquiring the values of the oxidation current intensity over time at constant potential values (established according to E_{OCP} , at anodic polarization), the recorded variations being correlated with the corrosion rate of the metal sample subjected to tests in the 3 corrosive environments. The metal samples on which the corrosion tests were performed in the three aggressive environments were made of carbon steel bars (with a diameter of 1 cm) of type, the active surface of the tested samples being 0.785 cm². Before exposure to corrosion, the active surface of the working electrode was sanded using 800 to 2400 grit SiC paper, then washed with distilled water, subjected to ultrasonic cleaning, cleaned in acetone and then dried.

Before performing each experiment, the working electrode was stabilized for 60 minutes, following the evolution of the corrosion potential over time. In order to observe whether the valerian extract undergoes transformations in the potential window between the release of hydrogen or oxygen, cyclic voltammetry experiments were performed at valerian tincture concentrations of 2.5 mL L⁻¹ and 10 mL L⁻¹ respectively on the platinum electrode, starting from the open circuit potential. Next, the potentiodynamic polarization curves were obtained for inhibitor concentrations of 1; 2.5; 5 and

10 mL L⁻¹, on a potential range between -250 mV and +250 mV compared to E_{OCP} , at a polarization speed of 1 mV s⁻¹. Thus, in order to obtain more details about the kinetics of the corrosion process for the tested samples, chronoamperometric measurements were performed for 15 minutes at two different values of the oxidation potential value, +25 mV vs. E_{corr} , respectively +250 mV vs. E_{corr} in the most aggressive solution.

The corrosion parameters were obtained by fitting of the linear polarization curves recorded, using BioLogic Potentiostat SP-150 Software. Also, the polarization resistances (R_p) were calculated from the Stern-Geary equation (3) [22,27]:

$$R_p = b_a \cdot b_c / [i_{corr} \cdot 2.303 \cdot (b_a + b_c)] \quad (3)$$

where:

R_p is the polarization resistance, Ω cm²;
 b_a and b_c represents the anodic and cathodic Tafel slopes, V
 i_{corr} is the corrosion current, A cm⁻².

In order to determine the inhibition efficiency from Tafel slope method was used the equation (4) [22,28]:

$$IE [\%] = [(i_{corr} - i_{corr(inh)}) / i_{corr}] \cdot 100 \quad (4)$$

where: i_{corr} and $i_{corr(inh)}$ are corrosion current densities in the absence and in the presence of the valerian tincture, A m⁻².

Molecular modelling

The first two most prevalent compounds present in the studied *Valeriana officinalis* extract (*i.e.* Bornyl acetate, BA and alpha Fenchene, AF) have been subjected to a conformational analysis and subsequent calculation of specific molecular descriptors. Geometries of BA and AF have been optimized in the gas phase. The specified molecular descriptors (frontier orbital energies, dipole moment, molecular hardness/softness, ionization energies, electron affinities, etc.) have been calculated by employing the Becke,3-parameter, Lee–Yang–Parr (B3LYP) [20,21] density functional method alongside the 6-31G* basis set.

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