Arabian Journal of Chemical and Environmental Researches

Vol. 07 Issue 2 (2020) 126–143

Effect of substitution on corrosion inhibition properties of three Imidazole derivatives on mild steel in 1M HCl

M. Bouklah[1*], H. Elmsellem[1], O. Krim[1], G. Serdaroğlu[2*], B. Hammouti [1], A. Elidrissi [1], S. Kaya[3], I. Warad [4]

[1] *LCAE-URAC18, Faculty of Science, University Mohammed Premier, B.P. 717, 60000 Oujda, Morocco*

e-mail: boukmmm@yahoo.fr, h.elmsellem@gmail.com, ouassini72@gmail.com, b1.hammouti@ump.ac.ma, ab.elidrissi@yahoo.fr

[2] *Sivas Cumhuriyet University, Faculty of Education, Math. and Sci Edu., 58140, Sivas/Turkey*

e-mail:goncagul.serdaroglu@gmail.com

[3] *Sivas Cumhuriyet University, Health Services Vocational School, Department of Pharmacy, 58140, Sivas/Turkey*

e-mail: savaskaya1989@gmail.com

[4] *Department of Chemistry and Earth Sciences, PO Box 2713, Qatar University, Doha, Qatar ;*
e-mail: ismail.warad@qu.edu.qa

Received 28 September 2020, Revised 22 Oct 2020, Accepted 24 Oct 2020

Abstract

In this paper, we study the effect of substitution of three imidazoles: 1-vinyl-1H-imidazole (VyIm); 1-(2-Dodecylsulfanyl-ethyl)-1H-imidazole (DEEIm) and 2-Imidazol-1-yl-ethylsulfanyl)-acetic acid (ImESAA) on adsorption properties on the steel surface in molar HCl solution. The investigation was performed using weight loss data combined to theoretical parameters deduced from dynamic simulation. Various kind of Langmuir, Temkin, Frumkin, Freundlich, Flory-Huggins and El-Awady were investigated and discussed. The higher inhibition efficiency of DEEIm was explained by the length aliphatic chain leading to reinforce charge on sulfur atom and imidazole ring. Free enthalpy and other data deduced from isotherm kinds help to understand adsorption process. The DFT calculations were performed to estimate the chemical reactivity of the VyIm, ImESAA and DEEIm compounds at B3LYP/6-311++G(df,pd) level.

Keywords: Imidazole; Corrosion; inhibitors; Adsorption; DFT; Dynamic Simulation spectroscopy

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*Corresponding author.
*E-mail address:*h.elmsellem@gmail.com ; goncagul.serdaroglu@gmail.com

1. Introduction

Hydrochloric acid is widely used in various industrial processes such as oil well acidification, acid pickling, descaling etc… Metallic materials used in these processes suffer seriously from electrochemical corrosion as well as hydrogen embrittlement to the metallic structure [1-3]. Due to its high tensile strength, ductility, malleability and above all, easy availability, mild steel stays the most used metallic materials. Last few decades have witnessed gradual surge in the works related to managing the acid induced corrosion damage of mild steel. Among various modes of operation in this field, application of various organic inhibitors remains one of active fields of research, mostly due to cost-effectiveness as well as easy applicability [4-6]. Organic corrosion inhibitors, by being adsorbed on the metal surface, create a barrier against diffusion of aggressive species toward metal surface, and thereby hindering its corrosion. Heteroatoms, such as O, N, S or P, as well as unsaturated bonds present in the organic molecule are reported to play the pivotal role during adsorption process by providing the non-bonded electrons for bond formation between the organic molecule and the metal surface [7-9]. In addition, overall spatial orientation of the inhibitor molecule also casts its own effect in dictating the extent of adsorption and subsequent corrosion inhibition propensity [10-12].

Moreover, nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors [7]. Among these, imidazole and its derivatives have been found to be the most effective and widely used organic compounds for corrosion inhibition of mild steel in acid medium [13–15] due to the presence of the electron donating heteroatom namely, nitrogen. In addition, the compounds containing both nitrogen and sulphur can provide excellent inhibition compared with compounds containing only nitrogen or sulphur [16-18]. Their adsorption is generally explained by the formation of an adherent film on the metal surface [19].

Besides, the quantum chemical descriptors have been calculated using the frontier molecular orbital (FMO) energies. The HOMO & LUMO and MEP plots have been used for showing the reactivity site and type of each compound. The possible intramolecular interactions, which contribute to the stabilization of each compound, existing on each compound have been determined by the results of the second-order-perturbative energy analysis and evaluated [20-22].

In continuation of our effort in developing corrosion inhibitors with high effectiveness and efficiency, the present paper, imidazole derivatives were synthesized using radical catalyzed addition of mercaptoacetic acid and 1-dodecanethiol to 1-vinylvinylimidazole, as described elsewhere [23]. The properties of these compounds; VyIm, DEEIm and ImESAA, as corrosion inhibitors for mild steel in molar HCl were studied by gravimetry combined to theoretical parameters deduced from DFT simulation.

2. Materials and methods

2.1) Materials & Synthesis

The chemical composition (wt.) of the Mild steel (MS) used in the present study was 0.09 wt.% P, 0.38 wt.% Si, 0.01 wt.% Al, 0.05 wt.% Mn, 0.21 wt.% C, 0.05 wt.% S. Corrosion media were prepared from HCl and double-distilled water. The synthesis of Dodecylsulfanyl-ethyl)-1H-imidazole (DEEIm) and (2-Imidazol-1-yl-ethylsulfanyl)-acetic acid (ImESAA) from the commercial compound 1-vinylvinyl-imidazole as described in [23].

2.2) Weight loss technique

Gravimetric experiments were carried out in a double-walled glass cell. The test pieces were cut nearly (1.5 cm x 1.5 cm x 0.04 cm), Weighed and suspended in the test solution (1M HCl) with and without the addition of the inhibitors at a temperature of 308 K in air atmosphere without bubbling. After specified periods of time (6h), the test pieces were taken out of the test solution, rinsed in doubly distilled water, dried as before and weighed again. The inhibition efficiency E_w was calculated using the following equation:

$$E_W\,\% = \frac{W^0_{corr} - W_{corr}}{W^0_{corr}} \times 100 \qquad \textbf{Eq.1}$$

W_{corr} and W^0_{corr} are the corrosion rates of MS in the presence and absence of inhibitor, respectively.

2.4) Theoretical Method

All DFT calculations were conducted using G09W [24] package, at B3LYP/6-311++G(df,pd) level [25,26]. The optimized structures of the VyIm, ImESAA, and DEEIm compounds on the ground state compounds were proved by the absence of imaginary frequency in the force constant method. Based on the DFT theory [27-31], the electronegativity (χ), electronic chemical potential (μ), hardness (η), electrophilicity index (ω) and charge transfer capability (ΔN) at a constant external potential can be calculated with the following equations:

$$\mu = -\chi = \left[\frac{\partial E}{\partial N}\right]_{\nu(r)} = -\left(\frac{I+A}{2}\right) \qquad \textbf{Eq.2}$$

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{\nu(r)} = \frac{I-A}{2} \qquad \textbf{Eq.3}$$

$$\omega = \chi^2 / 2\eta = \mu^2 / 2\eta \qquad \textbf{Eq.4}$$

NBO analysis was performed to estimate the possible intramolecular interactions as a resulting of the electron movement to an antibonding orbital from a donor orbital [32,33].

3. Results and discussion

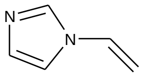
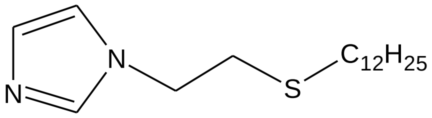
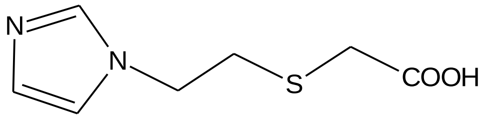
3.1. Gravimetric measurements

Concentrations effect

Corrosion rate and inhibition efficiency results derived from weight loss tests performed during 6 hours are reported in Table 1, [23]. The addition of imidazole compounds at all concentrations tested decreased the corrosion reaction, In other words, imidazoles inhibit the MS corrosion in HCl solution, their efficiency increases according to the following sequence :

E%(VyIm) < E%(ImESAA) < E%(DEEIm)

Table 1 Gravimetric results of mild steel in 1M HCl at 308 K at different inhibitor concentrations [23].

structures of inhibitors	Concentration (M)	W_{corr} (mg.cm^{-2} .h^{-1})	E_W (%)
	Blank	1.1	-
VyIm  ($C_5H_6N_2$; M=94,1g.mol^{-1})	10^{-3}	0.270	75.5
	5 x 10^{-4}	- - -	- - -
	10^{-4}	0.505	54.1
	5 x 10^{-5}	- - -	- - -
	10^{-5}	0.707	35.7
	10^{-6}	0.826	24.9
DEEIm  ($C_{17}H_{32}N_2S$; M=296,5g.mol^{-1})	10^{-3}	0.055	95.0
	5 x 10^{-4}	0.128	88.4
	10^{-4}	0.241	78.1
	5 x 10^{-5}	0.273	75.2
	10^{-5}	0.497	54.8
	10^{-6}	0.708	35.6
ImESAA  ($C_7H_{10}N_2O_2S$; M=186,2g.mol^{-1})	10^{-3}	0.149	86.5
	5 x 10^{-4}	0.213	80.6
	10^{-4}	0.332	69.8
	5 x 10^{-5}	0.427	61.2
	10^{-5}	0.510	53.6
	10^{-6}	0.602	45.3

The high values of inhibition efficiency observed in the presence of DEEIm and ImESAA are due to the presence of the sulfur atom and its highest molecular size compared to VyIm.

The nitrogen and sulfur atoms are the major adsorption center for their interaction with the metal surface. The heteroatoms S and N transfer their electrons (charge) to the metallic d-orbitals and form strong metal protective covering through coordinate bonding. The difference between DEEIm and ImESAA (E% reaches 95% and 86.5%, respectively at 10^{-3}M for example) can be explained by the length of aliphatic chain containing eleven –(CH_2), leading to the formation of hydrophile-hydrophobic molecule. The $(CH_2)_{11}$-CH_3 reinforces the electron density both on sulfur and aromatic ring. The length of aliphatic chain is widely discussed in Literature [34-39]. On the other hand, the inductive donor effect of -$(CH_2)_{11}$-CH_3 promotes the adsorption of DEEIm on the metal surface, while the inductive attracting effect of -COOH decreases the adsorption and therefore a decrease in the inhibitory efficacy.

3.2. Determination of adsorption type

To obtain more insight regarding the type of isotherm corresponding to the corrosion inhibitors molecules understudy during corrosion inhibition process, adsorption isotherm analyses were performed.

Corrosion inhibition occurs by adsorption at the metal surface. The inhibition efficiency depends on the type, number of active sites at the metal surface, charge density, molecular size of inhibitor, metal-inhibitor interactions and the metallic complex formation [40-42]. Adsorption isotherms give information on the metal inhibitor interactions [42]. Adsorption isotherms are very important in determining the mechanism of concurrent or competitive reactions issued from electrochemical and adsorption phenomena, the most frequently used are those of Langmuir, Temkin, Freundlich, Frumkin, Parsons, Flory –Huggins and Bockris – Swinkels. All these isotherms are of the general form :

$$f(\theta,x)e^{(-2a\theta)} = kc \qquad \textbf{Eq.5}$$

where, f (θ ,x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, c is the inhibitor concentration in the electrolyte, x is the size ratio indicating the number of water molecules displaced by one molecule of organic inhibitor, a is the molecular interaction parameter and k is the equilibrium constant for the adsorption.

Adsorption of inhibitor onto a metal surface is regarded as a substitutional reaction between the water molecule on the surface of the metal and the organic inhibitor as introduced by Bockris [43]. This substitutional reaction is equivalent to a chemical reaction as follows:

$$Inh_{solution} + n\,H_2O_{electrode} \rightarrow \; Inh_{electrode} + n\,H_2O_{solution}$$

Electrochemical measurements showed that all these imidazole compounds acted as cathodic domain i.e. inhibited the reduction of hydrogen ion at the surface [23]:

$$H^+_{solution} \rightarrow H^+_{surface} + e^- \rightarrow \frac{1}{2}H_2$$

To this end, several adsorption isotherms models, including Langmuir, Temkin, Frumkin, Freundlich, Flory-Huggins and El-Awady have been tested. The linear equations of various isotherms were regrouped in Table 2.

The different adsorption isotherms were fitted for all inhibitors, the surface coverage (θ) values were acquired from the weight loss data. Figure 1 (a-c) summarize the six kinds of isotherms for the more efficient inhibitor, DEEIm. The most important thermodynamic adsorption parameter, adsorption free energy (ΔG_{ads}), is estimated. The relationship between the adsorption constant, K, and the free energy of adsorption, ΔG_{ads}, is shown in the equation and corresponding results are listed in Table 3:

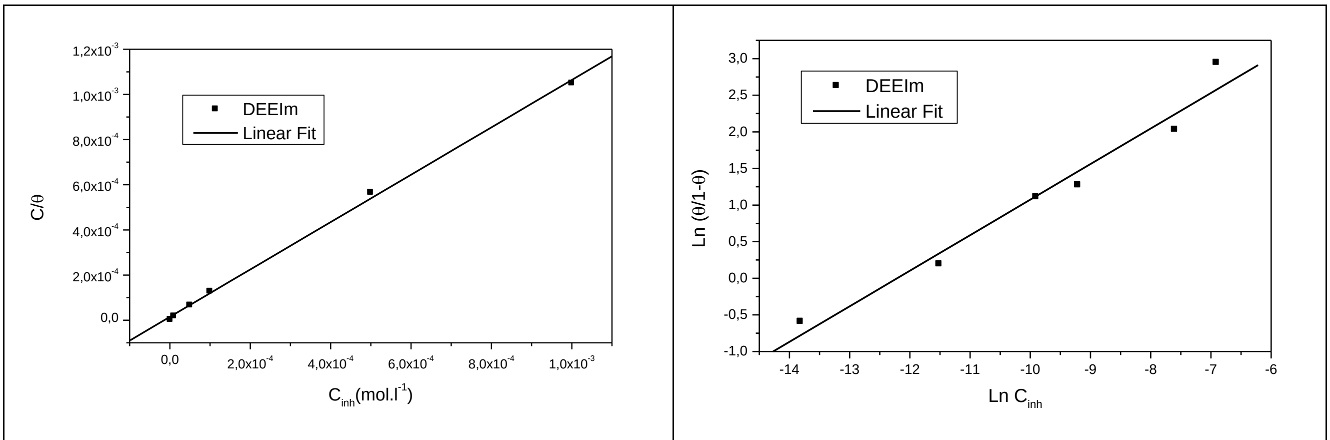
$$\Delta G_{ads} = -\,RT\,Ln\,(K_{ads}\,55.5)$$

where R is gas constant, T is temperature, 55.5 is the molar concentration of water in solution and K is the binding constant. The calculated values of K_{ads} are given in Table 3.

Table 2. Linear equations of different isotherms tested

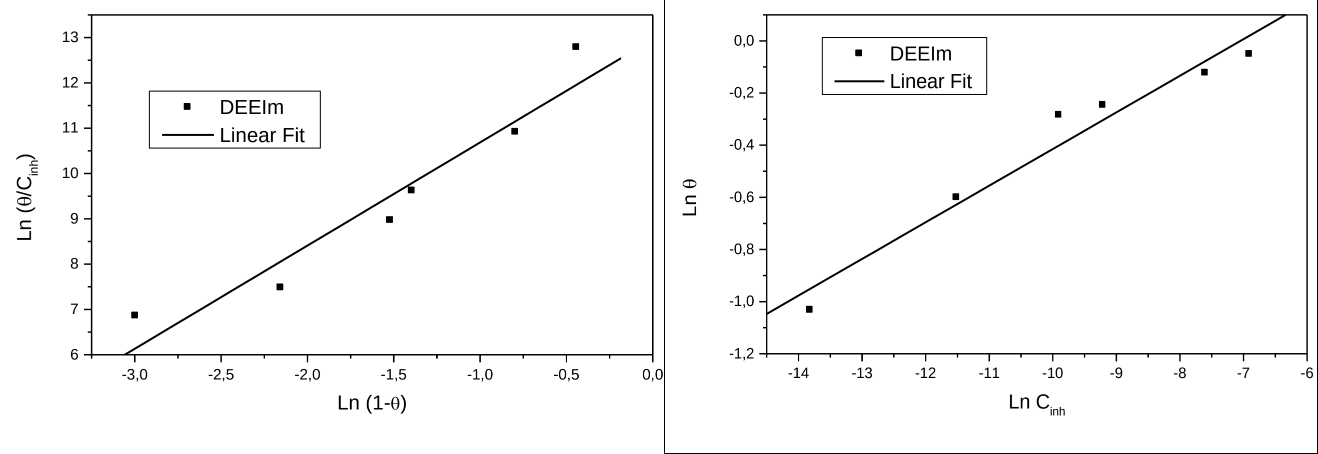
Isotherms	Linear equations	Descriptions
Langmuir	$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh}$ **Eq.6**	K: Coefficient of adsorption C_{inh}: inhibitor Concentration. Ө: Inhibitor recovery rate.
El-Awady	$\ln\left(\frac{\theta}{1-\theta}\right) = y\ln K + y\ln C_{inh}$ **Eq.7**	1/y is the number of water molecules removed by one molecule of inhibitor compound.
Flory-Huggins	$\ln\left(\frac{\theta}{C_{inh}}\right) = \ln K + x\ln(1-\theta)$ **Eq.8**	x is the value of adsorbed H_2O molecules replaced by inhibitors compounds.
Freundlich	$\ln\theta = \ln K + Z\ \ln C_{inh}$ **Eq.9**	0 < Z < 1: the adsorption of inhibitor on the surface of metal is easily. Z = 1: moderate adsorption of inhibitor on the metal surface. Z > 1: difficult adsorption behavior of inhibitor
Frumkin	$\ln\left(\frac{\theta}{(1-\theta)C_{inh}}\right) = \ln K + 2a\theta$ **Eq.10**	d represent the interaction factors among adsorbed molecules (repulsion or attraction force).
Temkin	$\theta = \frac{-1}{2a}\ln(K) - \frac{1}{2a}\ln(C_{inh})$ **Eq.11**	a is the repulsion or attraction interaction coefficient among adsorbed compounds

K_{ads} shows the interaction strength between the adsorbate and adsorbent in the electrolyte. Higher values of K_{ads} indicate effective adsorption of inhibitor molecules on the metal surface and high inhibition efficiency. The values of the free energy of adsorption (ΔG_{ads}) are negative in our case of the inhibitors. Negative values mean spontaneous adsorption of inhibitory molecules and stability of the adsorption layer. Generally, ΔG_{ads} values below -20 kJ mol-1 are consistent with an electrostatic interaction between charged molecules and a charged metal surface, indicating physical adsorption (physisorption). The chemisorption observed when the values of ΔG_{ads} are more negative than 40 kJ mol^{-1} involves the sharing or the transfer of charge of the inhibitory molecules on the metal surface to form a type of dative bond [44-46].



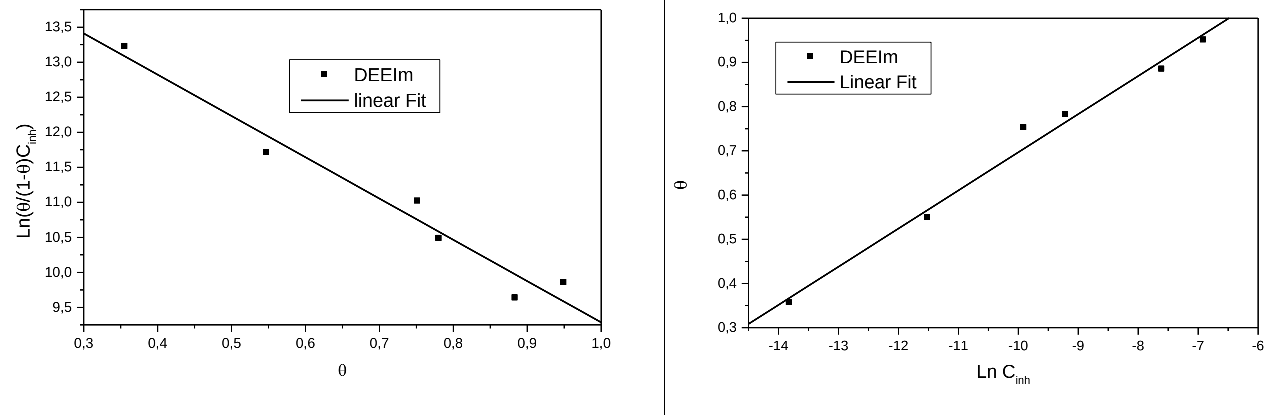
Langmuir isotherm

El –Awady isotherm



Flory-Huggins isotherm

Freundlich isotherm



Frumkin isotherm

Temkin isotherm

Figure 1: Various isotherms of inhibitor DEEIm on mild steel in HCl media.

The examination of curves and deduced values gathered in Table 3 revealed that inhibitors adsorbed on the surface of M steel. The R^2 values for each isotherm were used to justify the most suitable model. The best and simple isotherm Langmuir gave the best fitting of the rearranged relation with R^2 about 0.99.

Table 3. adsorption parameters of imidazole compounds using the six isotherms

Inhibitor	**K_{ads} (1M)**	**-ΔG_{ads} (kJ/mol)**	**R^2**	**Slope % or a or Z parameters**
VyIm				
Langmuir	2.774. 10^{4}	36.42	**0.996**	% = 1.3151
El-Awady	1.9154. 10^{4}	35.47	0.969	y = 0.31655
Flory-Huggins	3.4898.10^{5}	42.89	0.894	x = 4.8195
Freundlich	2.283	12.37	**0.996**	Z = 0.1609
Frumkin	1.805 10^{6}	47.09	0.934	a = -4.521
Temkin	2.024 10^{7}	53.27	0.969	a = -6.9262
DEEIm				
Langmuir	6.771 10^{4}	38.70	**0.999**	% = 1.049
El-Awady	2.011 10^{5}	41.47	0.966	y = 0.4860
Flory-Huggins	4.268 10^{5}	43.40	0.921	x = 2.2781
Freundlich	2.6935	12.80	0.954	Z = 0.1406
Frumkin	3.911 10^{6}	49.07	0.961	a = -2.9465
Temkin	7.052 10^{7}	56.46	0.986	a = -5.793
ImESAA				
Langmuir	5.640 10^{4}	38.24	**0.999**	% = 1.156
El-Awady	2.421 10^{5}	41.96	0.930	y = 0.2936
Flory-Huggins	1.450 10^{6}	46.53	0.877	x = 4.0237
Freundlich	1.983	12.01	0.987	Z = 0.0959
Frumkin	5.541 10^{7}	55.84	0.912	a = -5.4787
Temkin	9.724 10^{8}	63.17	0.964	a = -8.2142

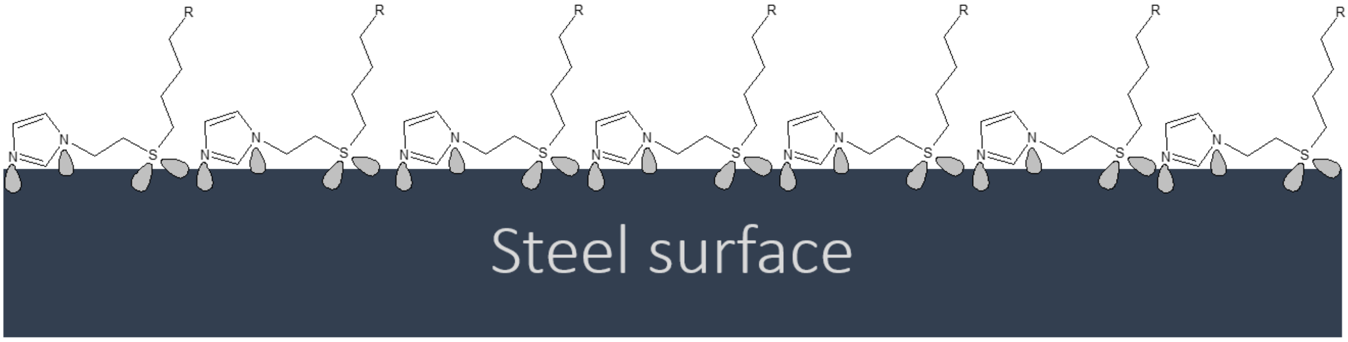
Discussion reposes on the different assumptions on which each adsorption isotherm is based. Langmuir (1918) was the first to propose a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint, that is there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium [47]. The assumptions of the Langmuir model are :

1. Surface is homogeneous, that is adsorption energy is constant over all sites,
2. Adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites,
3. Each site can accommodate only one molecule or atom,

but the slope deviated from unity indicating that adsorption is not ideal in the case of VyIm and inhibitor's molecules interact at the metal surface with each
other on non-homogenous surface.

The Freundlich adsorption isotherm was proposed by Freundlich in 1906 as an empirical equation, but it is consistent with the thermodynamics of heterogeneous adsorption [47]. Table 2 indicated that $0 < Z < 1$: the adsorption of inhibitor on the surface of metal is easily.

Indeed, the reciprocal of 'y' obtained from El-Awady isotherm is between 2 and 3; approximately equal to the value of size parameter 'x' deduced from Flory–Huggins isotherm implying that two to four water molecules have been replaced by one imidazole molecule in the course of the inhibition process as schematized by :



Scheme : proposal adsorption of imdazole molecule on the metal surface

Examination of other isotherms indicated that the imidazole adsorption process also can be regarded to obey the Temkin and Frumkin isotherms (**R^2=0.9**) which an indication of the existence of molecular interaction in the adsorbed layer, that non-totally ideal as suggested by Langmuir isotherm (slope slightly higher 1. These findings are further consolidated by the negative sign of the intermolecular interaction parameter in the adsorption layer 'a' of Temkin isotherm and the negative sign of the interaction parameter between molecules adsorbed on the metal surface 'a' of Frumkin isotherm, indicating highly repulsive lateral interactions in the adsorbed layer.

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption on heterogeneous surface, in the sense that the adsorption energy is distributed and the surface topography is patch wise, that is sites having the same adsorption energy are grouped together into one patch (the adsorption energy here is the energy of interaction between adsorbate and adsorbent) [48-51]. ΔG_{ads} obtained indicated that imidazoles compounds adsorbed on the metal surface both as physical and chemical adsorption. It's noted that ΔG_{ads} values determined by Freundlich equation are lower than those obtained by the others isotherms [52].

3. 3. Quantum Chemical Identifiers

Table 4 represents the calculated reactivity identifiers of the VyIm, ImESAA, and DEEIm compounds. All quantum chemical values are determined in these following orders:

ΔE_{gap} (eV): ImESAA (8.1419) < DEEIm (8.1841) < VyIm (8.2268)

μ (eV): ImESAA (-4.0106) < VyIm (-3.9803) < DEEIm (-3.8417)

η (eV): ImESAA (4.0710) < DEEIm (4.0921) < VyIm (4.1134)

ε (eV): DEEIm (1.8033) < VyIm (1.9258) < ImESAA (1.9755)

ΔN (eV): DEEIm (0.9388) < VyIm (0.9677) < ImESAA (0.9852)

According to these ordering, the ImESAA molecule is found to be as the electronically stable more than the other compounds because μ value (-4.0106 eV) of this compound is predicted as the lowest electronic chemical potential among three compounds. Also, the η, ε, and ΔN values ordering of these compounds imply that the ImESAA is the chemical soft compound, has the highest electrophilicity character, and the best charge transfer capability. On the other hand, the dipole moment and polarizability tensor of three compounds have been calculated as follow:

DM (debye): VyIm (3.479471) < ImESAA (3.559060) < DEEIm (4.375671)

α (au): VyIm (71.090667) < ImESAA (119.365333) < DEEIm (239.486333)

Depending on the Minimum Polarizability Principle, it can be said that VyIm is determined as the most stable compound and this results also supported by the dipole moment and hardness values of the compounds. Also, the inhibition efficiencies of these compounds are supported by the calculated hardness, polarizability, and dipole moment quantities.

Table 4. Quantum Chemical Parameters of the VyIm, ImESAA, and DEEIm compounds at B3LYP/6-311++G(df,pd)

	VyIm	**ImESAA**	**DEEIm**
HOMO (-I)	-8.09376	-8.08151	-7.93376
LUMO (-A)	0.13306	0.06041	0.25034
ΔE (L-H)	8.2268	8.1419	8.1841
μ	-3.9803	-4.0106	-3.8417
η	4.1134	4.0710	4.0921
ε	1.9258	1.9755	1.8033
ΔN	0.9677	0.9852	0.9388
α (au)	71.090667	119.365333	239.486333
DM (debye)	3.479471	3.559060	4.375671

Additionally, the nucleophilic and electrophilic attack locations of three compounds are illustrated in Fig. 2. For the VyIm compound, both the HOMO and LUMO are distributed on the whole molecular surface. On the other hand, the HOMO for the ImESAA compound shows that the imidazole and acetic acid groups have no role in the nucleophilic attack reactions, while the LUMO of this compound is almost localized the acidic chain that is the electrophilic attack site. Besides, the HOMO of the DEEIm compound is positioned around the sulfanyl group and LUMO of this compound is mainly localized on the imidazole ring and partly on the sulfanyl group. Here, it can be noted that the dodecyl group of the DEEIm compound does not affect both the nucleophilic and electrophilic attack reactions. Also, the N atom for all compounds is covered by the red color indicating the negative electrostatic potential region for the electrophilic attacks. Furthermore, the dark blue color demonstrating the positive electrostatic potential for the ImESAA compound is surrounding the H atom of the hydroxyl group. The light blue color implies the moderate positive electrostatic potential value. As can be noticed from Fig. 2, the dodecyl group of the DEEIm compound does not affect the nucleophilic or electrophilic attack reactions because of the neutral electrostatic potential.

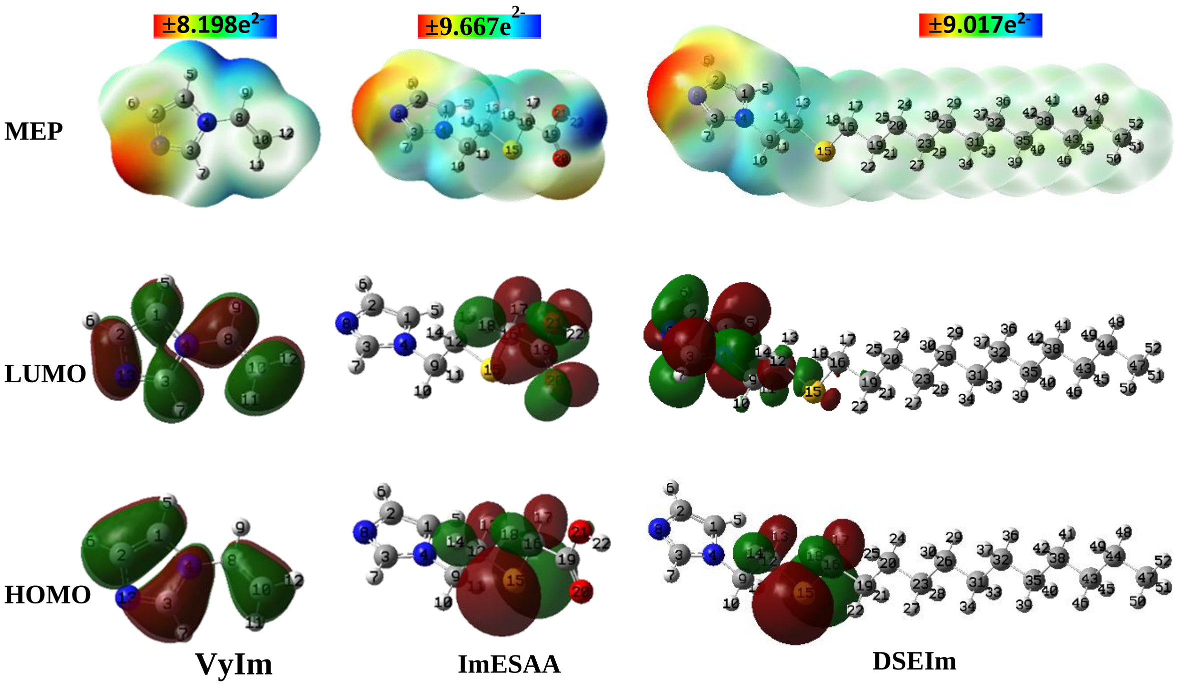


Fig. 2. HOMO & LUMO (isoval:0.02) and MEP (iso value:0.0004) plots of the VyIm, ImESAA, and DEEIm compounds using the B3LYP/6-311++G(df,pd) level

3.4. Natural Bond Orbital Analysis

The NBO analysis results of the VyIm, ImESAA, and DEEIm compounds are summarized in Table 5. As expected, the resonance interactions Π C1-C2 (2) → Π* C3-N13 and Π C3-N13 (2) → Π C1-C2 (2) have a great effect on the molecular stabilization of the VyIm compound; E$^{(2)}$ of these interactions are calculated in 21.60 and 27.93 kcal/mol, respectively. Similarly, the stabilization energy of the corresponding interactions for ImESAA and DEEIm compounds are calculated in 22.07/ 29.76 kcal/mol and 22.06/ 29.76 kcal/mol, respectively. The energy of the anomeric interaction LP (1) N13→ σ* C3-N4 for the VyIm compound is calculated as 9.14 kcal/mol. Furthermore, the energy of the interaction LP (1) N8→ σ* C3-N4 for ImESAA and DEEIm compounds are calculated in 8.76 and 8.72 kcal/mol, respectively.

Table 5. NBO analysis results for the VyIm, ImESAA, and DEEIm compounds using the B3LYP/6-311++G(df,pd) level

Donor(i)	ED$_i$/e	Acceptor (j)	ED$_j$/e	E(2)/ kcalmol^{-1}	E(j)-E(i)/ a.u	F(i.j)/ a.u
VyIm						
Π C1-C2 (2)	1.87246	Π* C3-N13	0.33550	21.60	0.38	0.085
Π C3-N13 (2)	1.87804	Π* C1-C2	0.27605	27.93	0.43	0.102
LP (1) N13	1.92916	σ* C3-N4	0.04144	9.14	0.93	0.083
ImESAA						
Π C1-C2 (2)	1.86387	Π* C3-N8	0.36926	22.07	0.37	0.086
Π C3-N8 (2)	1.87009	Π* C1-C2	0.29622	29.76	0.43	0.105
σ C16-H17 (1)	1.97439	Π* C19-O20	0.19392	5.59	0.67	0.057
σ C16-H18 (1)	1.97430	Π* C19-O20	0.19392	5.61	0.67	0.057
LP (1) N4	1.56749	σ* C9-H11	0.01689	3.32	0.75	0.050
		σ* C9-C12	0.01758	6.74	0.73	0.070
LP (1) N8	1.92651	σ* C3-N4	0.04144	8.76	0.95	0.082
LP (2) S15	1.93459	σ* C12-H13	0.02261	5.24	0.75	0.057
		σ* C12-H14	0.02252	5.16	0.75	0.056
		σ* C16-H17	0.02036	5.33	0.74	0.057
		σ* C16-H18	0.02034	5.34	0.74	0.057
DEEIm						
Π C1-C2 (2)	1.86372	Π* C3-N8	0.37130	22.06	0.37	0.086
Π C3-N8 (2)	1.86995	Π* C1-C2	0.29762	29.76	0.43	0.105
LP (1) N4	1.56508	σ* C9-H11	0.01714	3.37	0.75	0.050
		σ* C9-C12	0.01734	6.61	0.73	0.070
LP (1) N8	1.92677	σ * C3-N4	0.03849	8.72	0.95	0.082
LP (2) S15	1.93723	σ* C12-H13	0.022510.022	5.08	0.75	0.056
		σ* C12-H14	62	5.20	0.75	0.056
		σ* C16-H17	0.023550.023	5.01	0.75	0.055
		σ* C16-H18	28	4.81	0.75	0.054

* E$^{(2)}$ is the energy of hyper conjugative interaction (stabilization energy).

For the ImESAA compound, it is worth to notice that the electron movement to antibonding orbital Π* C19-O20 from each bond orbital of σ C16-H17 (1) and σ C16-H18 (1) is calculated with the energy of 5.59 and 5.61 kcal/mol. For the ImESAA and DEEIm compounds, the charge transfer from the lone pair electron of the N4 atom to each of antibonding orbital σ* C9-H11 and σ* C9-C12 have contributed to the stabilization energy with the energy of 3.32/6.74 kcal/mol and 3.37/ 6.61 kcal/mol, respectively. For the ImESAA, the energies of the anomeric interactions LP (2) S15 → σ* C12-H13, LP (2) S15 → σ*

C12-H14, LP (2) S15 → σ* C16-H17, and LP (2) S15 → σ* C16-H18 are calculated in 5.24, 5.16, 5.33, and 5.34 kcal/mol, respectively. Similarly, the corresponding energies calculated for the DEEIm compound are changed in the range of 4.81-5.20 kcal/mol. Here, these results have supported MEP plots, that is, the red color on the MEP plots for all compounds corresponds to the region where the electron delocalization occurs mostly.

Conclusion

In the present work, corrosion inhibition properties of three novel imidazole derivatives noted DEEIm; ImESAA and VyIm for mild steel in HCl medium were investigated experimentally and theoretically, and results were interesting. Based on the results presented in the present study, three imidazole derivatives acted as good corrosion inhibitors and their inhibition performance increased with concentration, reaching 95% for DEEIm ; 86% for ImESAA and 75 for VyIm 10^{-3} M at 308 K. Hence, DEEIm exhibited excellent inhibition performance.

The adsorption mode for two inhibitors DEEIm and ImESAA on mild steel surface followed Langmuir adsorption isotherm; on the other hand, the VyIm inhibitor followed by the Freundlich adsorption isotherm. As justified by the negative values of ΔG_{ads}, the adsorption mechanism of inhibitors is spontaneous, and their values reveal a combination of physical and chemical adsorption.

Computational calculation obtained through DFT analyses demonstrated that the imidazole molecules could be greatly adsorbed on the iron surface. Considering all quantum parameters, DFT findings were firmly in line with experimental findings

Acknowledgments: All calculations reported in this paper were performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources), TURKEY.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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