



Some new ionic liquids derivatives: Synthesis, characterization and comparative study towards corrosion of C-steel in acidic media

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ABSTRACT

Corrosion inhibition of C-steel in 1.0 M HCl was investigated in the absence and presence of different concentrations of some new ionic liquids derivatives namely, 1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide (MS35) and 3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H-imidazol-3-ium bromide (MS36) were synthesised and their inhibitive action against the corrosion of C-steel in 1.0 M HCl solution were investigated at 308 K using gravimetric measurements. Results show that MS35 is a good inhibitor and inhibition efficiency reaches 97.3% at 10⁻² M. The adsorption of these compounds on C-steel surface obeys Langmuir's adsorption isotherm. The kinetic and thermodynamic parameters for C-steel corrosion and inhibitor adsorption, respectively, were determined and discussed. The comparative study of inhibitive performance of the two new ionic liquids derivatives revealed that MS35 is more effective than MS36. Quantum chemical approach, using the density functional theory (DFT), was applied in order to get better understanding about the relationship between the inhibition efficiency and molecular structure of MS35 and MS36.

Keywords: Corrosion inhibition; Adsorption; C-Steel; Thermodynamic properties; gravimetric measurements.

INTRODUCTION

C-steel is the most widely used as constructional material in many industries due to its excellent mechanical and low cost. It is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment. Acid solutions are widely used in industry, e.g., chemical cleaning, descaling, pickling, and oil-well acidizing, which leads to corrosive attack. Therefore, the consumption of inhibitors to reduce corrosion has increased in recent years. The corrosion controls by inhibitors is one of the most common effective and economic methods to protect metals in acid media [1–19].

The majority of the well-known inhibitors are organic compounds containing heteroatom, such as O, N, or S and multiple bonds, which allow an adsorption on the metal surface [20–22]. The molecules that, at the same time,

contain nitrogen and sulphur in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only sulphur or nitrogen [23, 24]. Recently, Ionic liquids have been also widely investigated for a variety of applications [25–28]. In particular, the most extensively studied ILs is based upon the imidazolium cation. Imidazolium, pyridinium and pyridazinium-based ionic liquids are reported to show corrosion resistant behavior on copper [29, 30] and mild steel [31, 32]. It was found that the action of such inhibitors depends on the specific interaction between the functional groups and the metal surface, due to the presence of the $-C=N-$ group and electronegative nitrogen in the molecule.

The present work was established to study the corrosion inhibition of C-steel in 1.0 M HCl solution by new ionic liquids derivatives as corrosion inhibitors using weight loss method and theoretical studies. The effect of concentration on the inhibition efficiency has been examined. The thermodynamic parameters for dissolution processes were calculated and discussed. The chemical structures of the studied imidazolium ionic liquids are given in Fig 1.

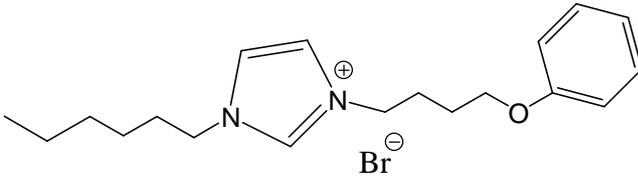
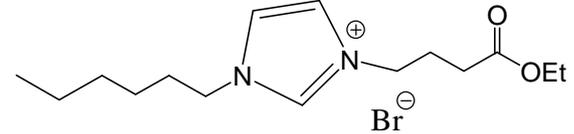
Abbreviation	Structural formula	Name
MS35		1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide
MS36		3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H-imidazol-3-ium bromide

Figure 1. The chemical structure of the studied imidazolium ionic liquids.

EXPERIMENTAL SECTION

Materials

The steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37 % HCl with double-distilled water. The concentration range of MS35 and MS36 employed was 10^{-6} M to 10^{-2} M.

Synthesis

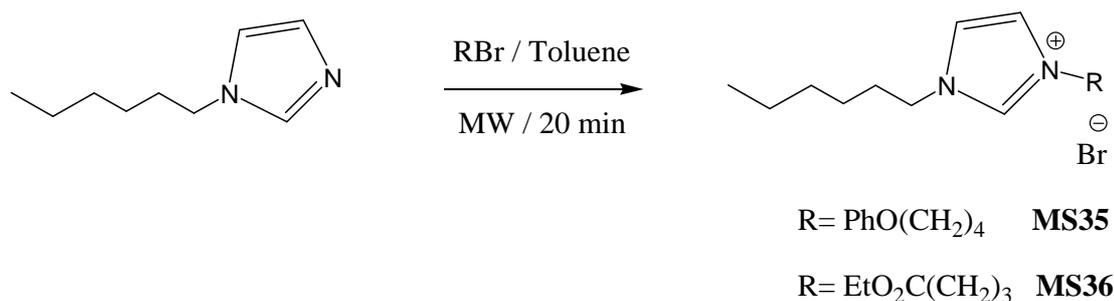
Measurements and equipments

All synthesized compounds were and characterized using ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopies. The spectra were obtained in DMSO at room temperature. Chemical shifts (δ) were reported in ppm to a scale calibrated for tetramethylsilane (TMS) as an internal standard. The LC-MS spectra were measured using a Micromass, LCT mass spectrometer. IR spectra were recorded in NaCl disc on a Shimadzu 8201 PC, FTIR spectrophotometer (\square_{max} in cm^{-1}). The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer as well as a pressure, temperature and power controls. The maximum operating pressure of the reactor is 20 bar. The power and temperature range are 15 - 300 W and 60 – 250 °C, respectively.

Microwave assisted synthesis of imidazolium-based ionic liquids

Many procedures are recommended for the Green Chemistry [33] involving: solvent-free reactions, non-classical modes of activation such as ultrasounds or microwaves. The use of MW irradiation leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach [34-37].

In continuation of our previous works, new eco-friendly imidazolium-based ionic liquids (MS35 and MS36) were prepared using microwave irradiation in short duration of time with quantitative yields [38, 39].



Scheme 1. Synthesis of new imidazolium-based ionic liquids under microwave irradiation (MW).

The nucleophilic alkylation of 1-hexylimidazole with two different functionalized alkyl halides afforded the corresponding imidazolium ionic liquids in 85-88% yield. (Table1)

Table 1. Different entries and reaction yields for the synthesis of imidazolium-based ionic liquids under microwave irradiation (MW).

Entry	RX	Yield (%)
MS35	PhO(CH ₂) ₄ Br	87
MS36	EtO ₂ C(CH ₂) ₃ Br	83

Synthesis of 1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide (MS35)

1-hexylimidazole (1g, 6.5 mmol), (4-bromobutoxy)benzene (1.64g, 7.2 mmol) and 00 mL of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 100°C. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 °C. The yield of MS35 was 87%. The product was analyzed using ¹H NMR, ¹³C NMR and LCMS. ¹H NMR (400MHz, DMSO). ¹H NMR δ: 1.29 (t, *J* = 7.2 , Hz 3H), 1.34 (quint, *J* = 7.2 , Hz 2H), 1.41 (m, 4H), 1.69 (quint, *J* = 7.6 Hz , 2H), 1.77 (quint, *J* = 7.6 Hz , 2H), 1.96 (quint, *J* = 7.6 Hz , 2H), 3.96 (t, *J* = 7.6 Hz , 2H), 3.72 (quint, *J* = 7.2 Hz , 2H), 4.29 (t, *J* = 7.6 Hz , 2H), 6.87-6.91 (m, 3H, Ar-H), 7.22 -7.27 (m, 2H , Ar-H), 7.93-7.99 (m, 2H), 9.55 (s, 1H), ¹³C NMR δ 15.0 (CH₃), 22.3 (CH₂), 26.3 (CH₂), 27.3 (CH₂), 31.6 (CH₂), 33.9 (CH₂), 44.1 (CH₂), 48.3 (CH₂), 52.4 (CH₂), 66.6 (CH₂), 114.3 (CH), 120.4 (CH), 122.1 (CH), 122.3 (CH), 129.4 (CH), 135.8 (CH), 158.3 (C) ; IR (□_{max} cm⁻¹) 1082 (C-O), LCMS (M-Br) 301 found for C₁₉H₂₉N₂O⁺.

Synthesis of 3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H-imidazol-3-ium bromide (MS36)

1-hexylimidazole (1g, 6.5 mmol), ethyl 4-bromobutyrate (1.41g, 7.2 mmol) and 10mL of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 100 °C. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 °C. The yield of MS36 was 83%. The product was analyzed with ¹H NMR, ¹³C NMR and LCMS. ¹H NMR (400MHz, DMSO) δ: 0.94 (t, *J* = 7.6, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.28 (m, *J* = 7.6, 2H), 1.33 (quint, *J* = 7.6, 2H), 1.82 (quint, *J* = 7.6, 2H), 1.97 (quint, *J* = 7.6, 2H), 2.14 (quint, *J* = 7.6, 2H), 2.25 (quint, *J* = 7.6, 2H), 3.99 (t, *J* = 6.8, 2H), 4.27 (q,t, *overlapping*, 4H), 4.46 (t, *J* = 6.8, 2H), 6.85-6.93 (m, 3H), 7.23-7.27 (m, 2H), 7.63 (d, 1H), 7.70 (d, 1H), 10.30 (s, 1H); ¹³C NMR (100MHz, DMSO) δ: 13.9 (CH₃), 14.9 (CH₃), 22.6 (CH₂), 24.8 (CH₂), 28.7 (CH₂), 30.1 (CH₂), 33.2 (CH₂), 44.1 (CH₂), 47.9 (CH₂), 51.1 (CH₂), 59.9 (CH₂), 122.1 (CH), 122.3 (CH), 135.9 (CH), 171.8 (C); IR (□_{max} cm⁻¹) 1726 (C=O), LCMS (M-Br) 267 found for C₁₃H₂₃N₂O₂⁺.

Weight loss measurements

The gravimetric measurements were carried out at the definite time interval of 6 h at room temperature using an analytical balance (precision ± 0.1 mg). The carbon steel specimens used have a rectangular form (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 50 mL of non-de-aerated test solution. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. Triplicate experiments were performed in each case and the mean value of the weight loss is calculated.

Quantum chemical calculations

All theoretical calculations were performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [40–42] with 6- 31G* basis set is implemented in Gaussian 03 program package [43]. This approach is shown to yield favorable geometries for a wide variety of systems. The following quantum chemical parameters were calculated from the obtained optimized molecular structure: the energy of the highest occupied molecular orbital (*E*_{HOMO}), the energy of

the lowest unoccupied molecular orbital (E_{LUMO}), the energy band gap ($\Delta E_{gap} = E_{HOMO} - E_{LUMO}$), the dipole moment (μ) and the total energy (TE).

RESULT AND DISCUSSION

Effect of inhibitors concentration

Weight loss of C-steel, in mg cm^2 of the surface area, was determined at different concentration in the absence and presence of the new ionic liquids derivatives (MS35 and MS36) at 308K. From the weight loss results, the corrosion rate (CR), the inhibition efficiency ($\eta_{WL}(\%)$) of the inhibitor and degree of surface coverage (θ) were calculated using equations 1, 2 and 3 [44, 45];

$$C_R = \frac{W_b - W_a}{At} \quad (1)$$

$$\eta_{WL}(\%) = \left(1 - \frac{w_i}{w_0}\right) \times 100 \quad (2)$$

$$\theta = 1 - \frac{w_i}{w_0} \quad (3)$$

where W_b and W_a are the specimen weight before and after immersion in the tested solution, w_0 and w_i are the values of corrosion weight losses of carbon steel in uninhibited and inhibited solutions, respectively, A the total area of the carbon steel specimen (cm^2) and t is the exposure time (h) and θ is the degree of surface coverage of the inhibitor.

The values of $\eta_{WL}(\%)$ for two inhibitors are given in Table 2. This show that the inhibition efficiency increases with the increasing inhibitor concentration. These results reveal that the compounds under investigation are fairly efficient inhibitors for C-steel dissolution in 1.0 M HCl solution. The inhibition of corrosion of C-steel by new ionic liquids derivatives can be explained in terms of adsorption on the metal surface. These compounds can be adsorbed on the C-steel surface by the interaction between lone pairs of electrons of nitrogen atoms of the inhibitors and the metal surface. This process is facilitated by the presence of vacant orbital of low energy in iron atom, as observed in the transition group elements. Careful inspection of these results showed that, the ranking of the inhibitors according to $\eta_{WL}(\%)$ is as follows: MS35 > MS36 for the same concentration. Compared with MS35 and MS36, the higher inhibition effect of MS35 may be attributed to the replacement of the group 4-ethoxy-4-oxobutyl in the position four by a group phenoxybutyl. In this way, a correlation between the electronic parameters (induction and mesomeric effects of the substituent and ionization potential values) as well as chemical structure (molecular area) and inhibition property is effective [46]. Also, the larger molecular size of MS35 can be considered which ensures greater coverage of the metallic surface [47, 48].

Table 2: Corrosion parameters obtained from weight loss measurements for carbon steel in 1.0 M HCl containing various concentrations of inhibitors at 308 K.

Inhibitors	Conc (M)	$10^{-4} \times CR$ ($\text{mg cm}^{-2} \text{h}^{-1}$)	$\eta_{WL}(\%)$	θ
Blank	1	4	-----	-----
MS35	10^{-6}	3.072	23.2	0.232
	10^{-5}	0.788	80.3	0.803
	10^{-4}	0.264	93.4	0.934
	10^{-3}	0.144	96.4	0.964
	10^{-2}	0.108	97.3	0.973
MS36	10^{-6}	3.472	13.2	0.132
	10^{-5}	3.036	24.1	0.241
	10^{-4}	2.572	35.7	0.357
	10^{-3}	0.568	85.8	0.858
	10^{-2}	0.252	93.7	0.937

Figs. 2 and 3 illustrate the variation of corrosion rate and efficiencies with concentration of inhibitor. It has been found off these compounds inhibits the corrosion of C-steel in HCl solution at all concentrations used in this study. It has also been observed that the inhibition efficiency for these compounds increases with the increase in concentration. Maximum $\eta_{WL}(\%)$ for these compounds were achieved at 10^{-2}M .

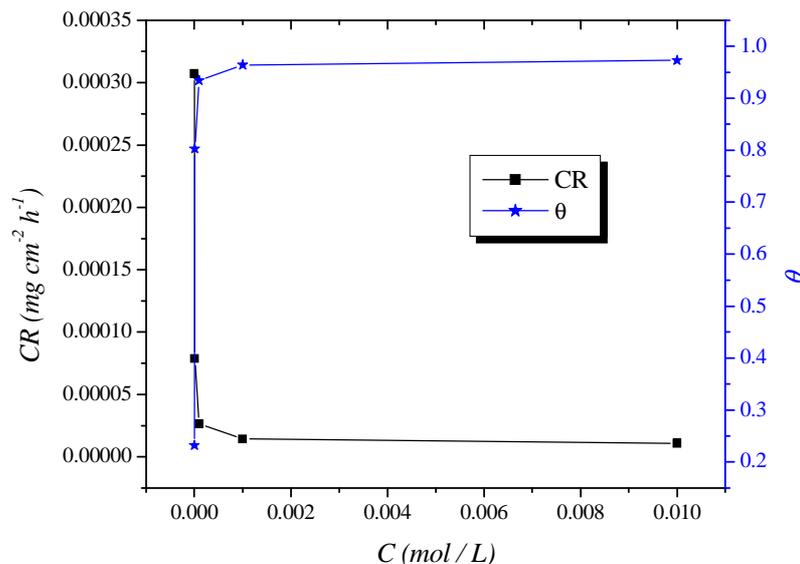


Figure 2. Variation of inhibition efficiency and corrosion rate in 1.0 M HCl on C-steel surface without and with different concentrations of MS35

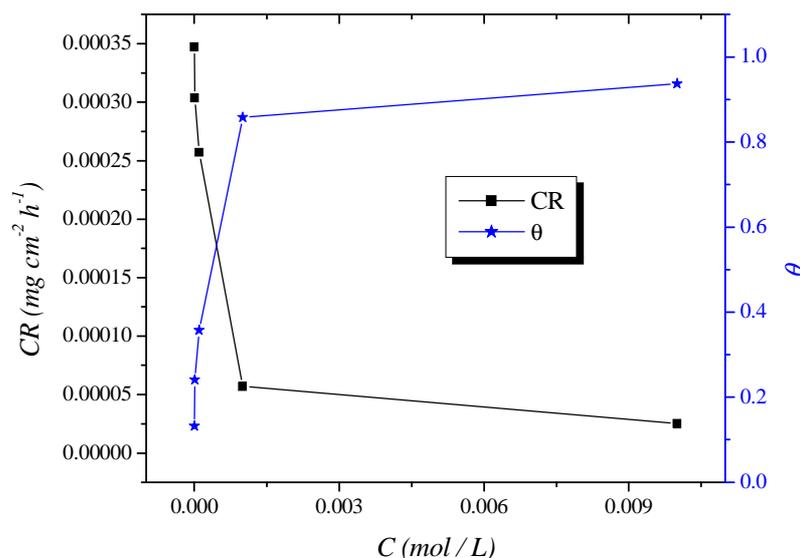
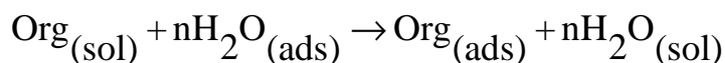


Figure 3. Variation of inhibition efficiency and corrosion rate in 1.0 M HCl on C-steel surface without and with different concentrations of MS36.

Adsorption isotherm and thermodynamic parameters

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [49]. The adsorption of an organic adsorbate at metal–solution interface can occur as a result of substitutional adsorption process between organic molecules presented in the aqueous solution (Org(sol)), and the water molecules previously adsorbed on the metallic surface (H₂O(ads)) [50]:



where Org(sol) and Org(ads) are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively, H₂O(ads) is the water molecule adsorbed on the metallic surface and n is the size ratio representing the number of water molecules replaced by one organic adsorbate. In order to obtain the adsorption isotherm, the degree of surface coverage, θ, for different concentrations of inhibitor in 1.0 M HCl solutions has been evaluated by the following equation (3).

The θ values are presented in Table 2. According to the Langmuir's isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation [51]:

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process. As seen from Fig. 4, the plot of C_{inh}/θ versus C_{inh} yields a straight line with a correlation coefficient more than 0.9999, showing that the adsorption of these inhibitors in acidic solutions is fitted to Langmuir adsorption isotherm. These results show that the inhibition of C-steel in HCl solutions by new ionic liquids derivatives is an adsorptive process. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions between the adsorbed species [52].

The K_{ads} values can be calculated from the intercept lines on the C/ θ -axis. This value is also related to the standard free energy of adsorption (ΔG_{ads}°), by the following equation [52, 53]:

$$\Delta G_{ads}^{\circ} = -RTLn(55.5K_{ads}) \quad (5)$$

where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant, ΔG_{ads}° is the standard free energy of adsorption, 55.5 is the concentration of water in the solution in mol dm⁻³, R is the universal gas constant and T is the absolute temperature in Kelvin.

The values of K_{ads} and ΔG_{ads}° for MS35 and MS36 in 1.0 M HCl solutions are given in Table 3. The negative sign of ΔG_{ads}° indicates that the inhibitors are spontaneously adsorbed on the metal surface [52, 54]. Generally, the magnitude of ΔG_{ads}° is around -20 kJ mol⁻¹ or less negative, which can be assumed that an electrostatic interaction exists between the inhibitor and the charged metal surface (i.e. physisorption). Standard free energy of adsorption (ΔG_{ads}°) around -40 kJ mol⁻¹ or more negative indicates that a charge sharing or transferring from organic species to the metal surface occurs to form a coordinate type of bond (i.e. chemisorption) [55, 56]. The calculated ΔG_{ads}° values for MS35 and MS36 in acid media show that an electrostatic interaction exists between the inhibitor and the charged metal surface while, as shown, chemisorption is more probable for MS35. It should be mentioned that the higher values of K_{ads} and ΔG_{ads}° refer to a higher adsorption and thus a higher inhibiting effect.

Table 3: Thermodynamic parameters for the adsorption of MS35 and MS36 in 1.0 M HCl on the C38 steel at 308K

Inhibitor	Slope	K_{ads} (M ⁻¹)	R ²	ΔG_{ads}° (kJ/mol)
MS35	1.02	207120.8	1.0000	-41.63
MS36	1.06	12752.8	0.9999	-34.49

Computational study

Gaussian program offers a wide variety of Density Functional Theory (DFT) models for discussions of DFT methods and applications. Energies, analytic gradients, and true analytic frequencies are available for all DFT models. This method serves also as efficient computational tools which can yield fast quantitative estimates for a number of properties. Highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}) and dipole moment (μ) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbital's (HOMO and LUMO) of reactants. E_{HOMO} is often associated with the electron donating ability of the molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower the value of E_{LUMO} , the more probable the molecule would accept electrons. A low value of the energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low. Consequently, less negative HOMO energy and smaller energy gap ($E_{HOMO} - E_{LUMO}$) are reflected in a stronger chemisorptions bond and perhaps greater protection efficiency. For dipole moment (μ), lower values of (μ) will favour accumulation of the inhibitor. Meanwhile, several authors state that the inhibition efficiency increases with increasing values of the dipole moment. On the other hand, survey of literature reveals that irregularities appeared in case of correlation of dipole moment with efficiency.

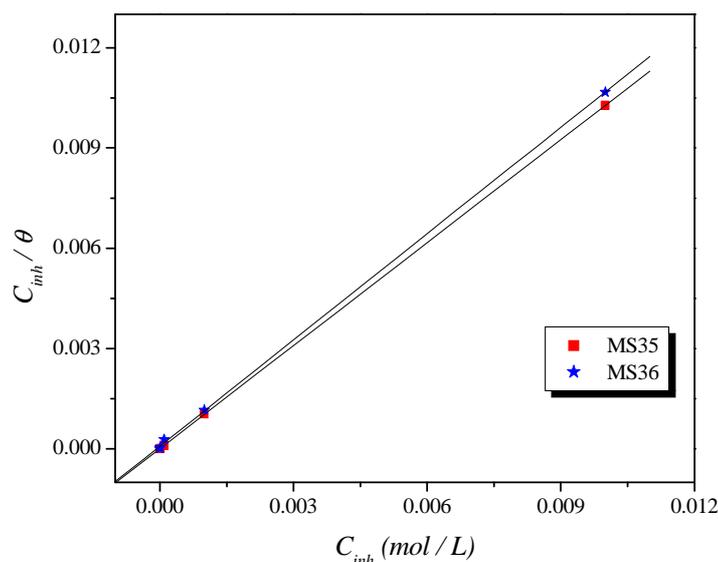


Figure 4. Langmuir adsorption of MS35 and MS36 on the steel surface in HCl solution.

Evaluation of the efficiency of MS36 and MS35 as corrosion inhibitor for C-steel in 1.0 M HCl has been performed using DFT method. The HOMO and LUMO electronic density distributions of these molecules were plotted in Figure 5. Note that for MS36, the HOMO resides on the two oxygens of a ethoxy-4-oxobutyl group of the studied compounds, but the LUMO resides on the protonated imidazol group. For MS35 the HOMO resides on the phenoxybutyl group of the studied compounds, but the LUMO resides on the protonated imidazol and phenoxybutyl group. The Mulliken charge density of MS36 and MS35 has been calculated and presented in Figure 5 and Table 4. There is a general consensus by several authors that the more negatively charged heteroatom, the more it can be adsorbed on the metal surface through donor-acceptor type reaction. From the values of Mulliken charge, there is an excess of negative charges in the Carbone atoms adjacent on nitrogen and oxygen atoms and heterocyclic groups, hence MS36 and MS35 molecules can be adsorbed on surface using these active centres leading to the corrosion inhibition effect.

Table 4 shows the quantum chemical calculation parameters (E_{HOMO} , E_{LUMO} , ΔE ($E_{LUMO} - E_{HOMO}$), dipole moment (μ), heat of formation and ionization potential) which have been calculated and correlated with experimental results. Note that a correlation exists between parameter quantum and the inhibition efficiency of MS36 and MS35. The less negative E_{HOMO} and the smaller ΔE reflect a great inhibition efficiency of MS35.

The inhibition of these compounds was determined experimentally by using both electrochemical polarization and weight loss techniques, and was found to be excellent inhibitors of steel corrosion. The decrease in the inhibition efficiency observed between 3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H-imidazol-3-ium bromide MS36 and 1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide MS35 is due to an effect of heteroatoms and heterocyclic groups. It is worth noting that the experiment showed that the substitute fixed on the imidazol of the 4-ethoxy-4-oxobutyl) for 4-phenoxybutyl does have much effect on the inhibition efficiency. Ultimately we can conclude for these imidazol derives Relationships between inhibition efficiency and the local quantum chemical parameters. The energy levels of frontier orbitals indicate the tendency to form bonds to the metal surface. Further study on chelation centre inhibitors requires information on the spatial distribution of the electron density of these compounds. The structure of molecules can affect the adsorption by influencing the electron density of the functional group. Finally we note a good agreement with the above mentioned experimental data obtained by weight loss and Quantum chemical calculation using DFT method by Gaussian program.

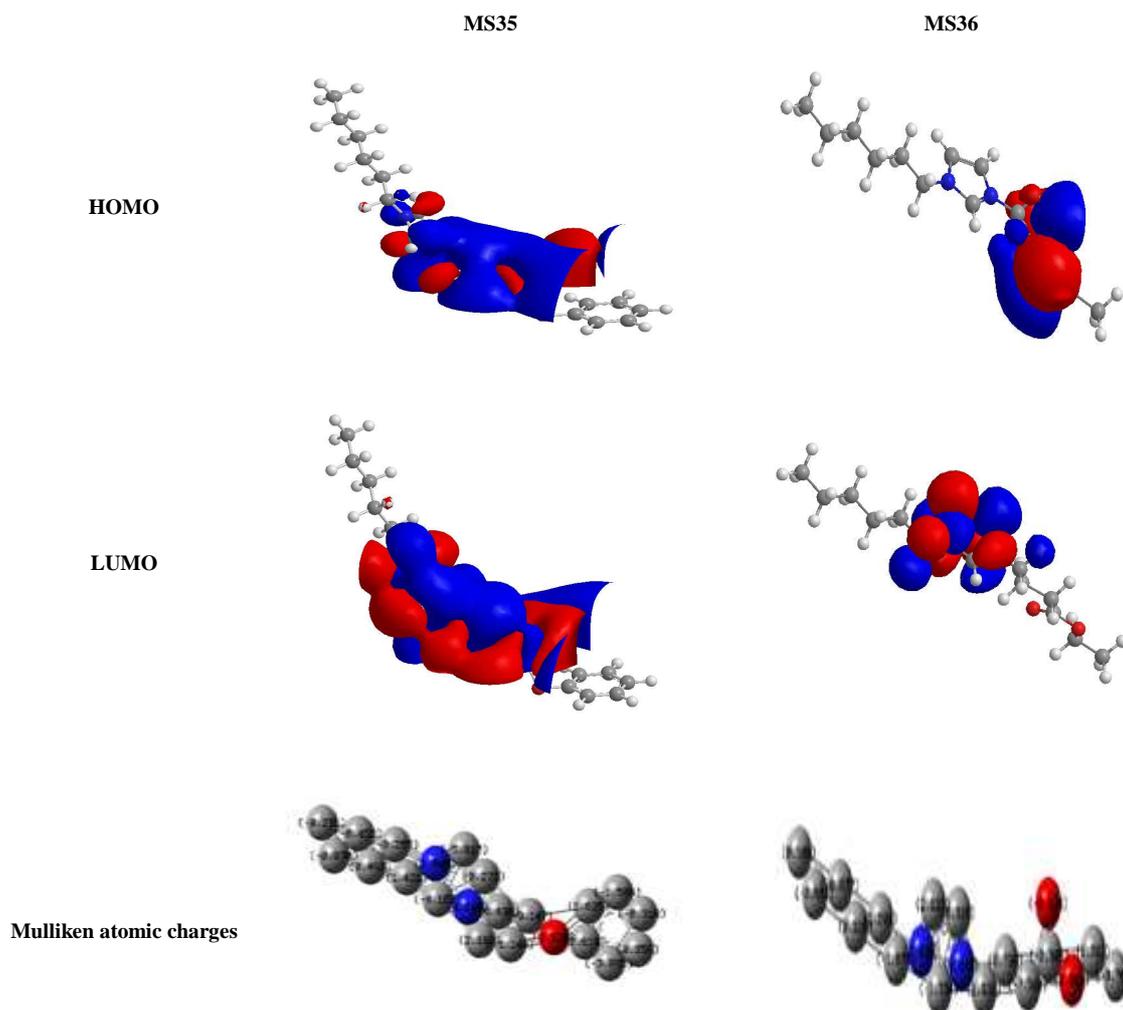


Figure 5. Molecular orbital plots and Mulliken atomic charges of MS36 and MS35

Table 4. The calculated quantum chemical parameters of MS35 and MS36

Compound	MS36	MS35
μ (Debye)	15.781	31.638
E_{HOMO} (eV)	-0.437	-0.421
E_{LUMO} (eV)	-0.423	-0.466
Gaps (eV)	0.014	0.045

CONCLUSION

Eco-friendly ionic liquids MS35 and MS36 have been successfully synthesized utilizing MW method with chemical yields of 85% and 88%, respectively. The inhibitive effect of the both used inhibitors in this method shows the good efficiency against the corrosion inhibition over C-steel. Inhibition efficiency increases with increasing inhibitor concentration. The adsorption of MS35 and MS36 on carbon steel surface is found to obey the Langmuir adsorption isotherm. The negative values of $\Delta G_{\text{ads}}^{\circ}$ indicate spontaneous adsorption of the inhibitor on the surface of steel. Quantum chemical approach was adequately used to explain the correlation between the inhibition of carbon steel corrosion and molecular structure of MS35 and MS36. It is found that the corrosion inhibition power of these new ionic liquids derivatives is closely related to its quantum chemical parameters.

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