Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 9, Page 3034-3045

http://www.jmaterenvironsci.com/

Electrochemical investigation and Quantum chemicalstudies on corrosion inhibition for ester-quats surfactants on iron in hydrochloricacid

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Received 17 Feb 2016,
Revised 18 Apr 2016,
Accepted 25 Apr 2016

Keywords

- ✓ *Ester-quat surfactant*
- ✓ *Iron*
- ✓ *Corrosion inhibitor*
- ✓ *Quantum chemical calculations*

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Abstract

The corrosion inhibition of iron in 1M hydrochloric acid solution in the presence of two ester quat surfactants; the mono ester quat: dodecanoyloxypropyl dodecyl dimethyl ammonium bromide (MEQ) and the Gemini ester quat: 1,3bis-(dodecanoyloxypropyl dimethyl ammonium) propane dibromide (GEQ) was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and surface analysis (SEM) techniques. Tafel curves showed that the corrosion current density decreases with addition of various concentrations of both inhibitors. However, it was noted that GEQ is more efficient than MEQ. Indeed, the inhibition efficiency of GEQ at 2.10^{-4}M reaches 96% against 87% for MEQ in acidic media. These surfactants act as good mixed inhibitors. EIS measurements showed that the studied compounds inhibit iron corrosion by adsorption of surfactant molecules on the iron surface. The effect of molecular structure on the inhibition efficiency was studied by theoretical methods (HF, DFT). Experimental and theoretical studies agree well and confirmed that GEQ is the best corrosion inhibitor.

1. Introduction

The issue of the effects of corrosion on structural integrity of metal surfaces has been a question of concern for some time. The use of chemical corrosion inhibitors is common in production and processing operations [1–5]. Nevertheless, the challenge is to develop a new class of corrosion inhibitors to protect the materials, which are environment friendly under various conditions. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [6-7].Organic inhibitors whose mode of action usually results in their adsorption on the metal surface are the most commonly used [8-9]. In general, two types of interaction describe adsorption: physical and chemical adsorption. It is accepted that the chemical adsorption process uses transfer or sharing of electrons between molecules of the inhibitor and the orbital "d" of the unsaturated metal surface to form, respectively coordination bonds or covalent bonds[10-11]. The transfer is improved by the presence of hetero atoms with free electron pairs [12-16].A large number of organic compounds have been studied as corrosion inhibitors for iron and its alloys in acidic environments[17-20]. Most of them are toxic to the environment, which led researchers to develop non-toxic inhibitors such as surfactants. Surfactants are chemicals used since prehistory. According to their use, they are known by different names such as detergents, emulsifiers, wetting agents, solubilizers, etc… Their applications range from beauty products to fabric softeners, mineral extraction and organic catalysis, inhibitors of corrosion etc... Thus, various surfactants are reported as good corrosion inhibitors: ionic surfactants [21-22], non-ionic surfactants [23]. Anew generation of surfactants called gemini or dimeric surfactants which are characterized by two hydrophilic heads and two hydrophobic tails have attracted the attention of researchers in recent years. The interest of this kind of surfactants is dealing with their important properties: low critical micellar concentration, considerable decrease in surface tension [24-

28]. Industry is always looking for more efficient products and the market is also guided by the price and the concern for the environment. The introduction of weak bonds such an ester bond into the surfactants in the series of ammonium quaternary improves their biodegradability [29]. Quantum theoretical calculations have been used recently as powerful tool to explain the corrosion inhibition mechanism [30-31]. The conceptual density functional theory (DFT) has been extensively used to correlate the inhibitive effect with the molecular structure and to analyze the characteristics of the interface inhibitor-metal mechanism [32-34]. In the frame of the theoric methods and based on the energy of the highest occupied molecular orbitals (E_{HOMO}) and lowest unoccupied molecular orbitals (E_{LUMO}), the chemical descriptors such as energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) absolute hardness (η), absolute softness (ρ), electronegativity (χ) and fraction of transferred electrons(ΔN) provides great contributions in the evaluation of quantum chemistry. Indeed they are highly successful in predicting the global chemical reactivity trends of the chemical compounds and consequently their effectiveness as corrosion inhibitors.

The objective of this study is to compare the inhibitive effect of two ester-quat surfactants (MEQ) and (GEQ) against the corrosion of iron in molar aggressive medium HCl, using the potentiodynamic polarization and electrochemical impedance spectroscopy methods. The samples surface of iron in the presence and absence of inhibitors were characterized by scanning electron Microscopy (SEM). This study was completed by quantum chemical calculations in order to correlate the inhibitory effect with the molecular structures of the compounds studied.

2.Experimental

2.1 Material

2.1.1 Metal

The metal tested in this study is an iron (99,5% purity), Ref LS 99376 J.Fe.000405/14 from good fellow CambridgeScience Park UK. The surface pretreatmentof the working electrode was carried out by grindingwith different grades of emery papers down to 1200 grit. The electrodewas then, rinsed with acetone, distilled water, and finallydipped in the electrolytic cell.A very good reproducibility of the experiments with this mechanical treatment was observed.

2.1.2 Inhibitors

The inhibitors studied are surfactants, named, the mono ester-quat (MEQ): dodecanoyl oxy propyl dodecyl dimethyl ammonium bromide and the gemini ester-quat (GEQ): 1,3-bis-(dodecanoyloxypropyl dimethyl ammonium) propane dibromide. The synthesis of these two compounds was carried out in our laboratory according to a procedure previously described[35-37]. The structure of these surfactants is presented in figure 1(a,b).

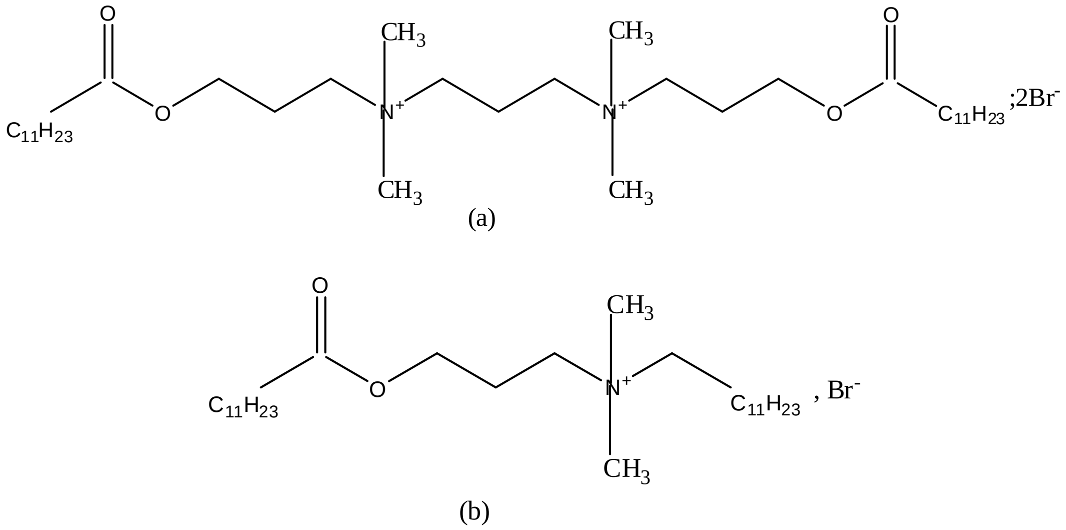


Figure 1: Structure of studied surfactants: (a)GEQ, (b)MEQ

2.1.3 Solution

The electrolyte is an aggressive solution 1M HCl, prepared from a commercial, hydrochloric acid solution (37%) and bidistilled water. For the inhibitive effect study, the concentration range used for two inhibitors is between $5x10^{-6}$ M and $2x10^{-4}$ M. The concentration range was chosen after the inhibitors solubility study in the corrosive medium. All solutions were prepared using bidistilled water.

2.2 Evaluation methods

2.2.1 Electrochemical measurements

The corrosion inhibiting properties were studied using electrochemical measurements. The measurements were performed at 25°C using a potentiostat / galvanostat and an electrochemical cell with three electrodes; an iron working electrode in square shape of $1cm^2$ area, a reference electrode (SCE) and a platinum electrode. To obtain steady state open circuit potential (E_{ocp}) the iron electrodes were immersed in the tested solution for 30 min before starting the measurements.The polarization measurements were carried out using a transfer function analyzer (Tacussel Radiometer PGZ301), which was controlled by a personal computer. The potential scan rate was 0.5mV/s. The polarization curve was recorded by polarization from -800mV to -200mV under potentiodynamic conditions corresponding to 1mV/s (sweep rate) and under air atmosphere. The electrochemical impedance spectroscopy measurements were realized in the frequency range from 100 KHz to 10 mHz at $E_{ocp}$with amplitude of 10 mV AC signal.In order to obtain the impedance parameters, the experimental data was fitted to the equivalent circuit model using the fit and simulation tool of the EC-LAB. Each test was repeated thrice in the same conditions, in the order to have an acceptable reproducibility.

2.2.2 Surface characterization

For morphological studies, Samples surface of iron were examined after exposure to 1M HClsolution for 24 hours in the absence and in the presence of ester-quat inhibitors at concentrations $2x10^{-4}$M.Microstructural investigations of the samples were carried out using the FEI quanta 450 FEG focused-ion-beam system, equipped with an EDAX Genesis energy dispersive spectrometer (EDS) at Moroccan Foundation for AdvancedScience, Innovation and Research (Mascir).

2.2.3 Quantum chemical study

In order to support the experimental data, theoretical calculations were conducted to provide molecular-level understanding of observed experimental behavior. In this context, we have performed our calculations by using the GAUSSIAN 09 set of programs [38] along with the graphical interface GaussView-5.0. Geometry optimization of the inhibitors was carried out by using two methods with basis set: HF/STO-3G(d) [39-41], HF/6-31 G(d) [42-46], DFT/B3LYP/STO-3G* [47-48].

3.Results and discussion

3.1 Polarization measurements

The measurements were achieved to determine the polarization curves parameters of the iron/electrolyte interface in presence of different concentrations of the inhibitors. Figure 2 shows the polarization curves of iron in absence and presence of the two surfactants.

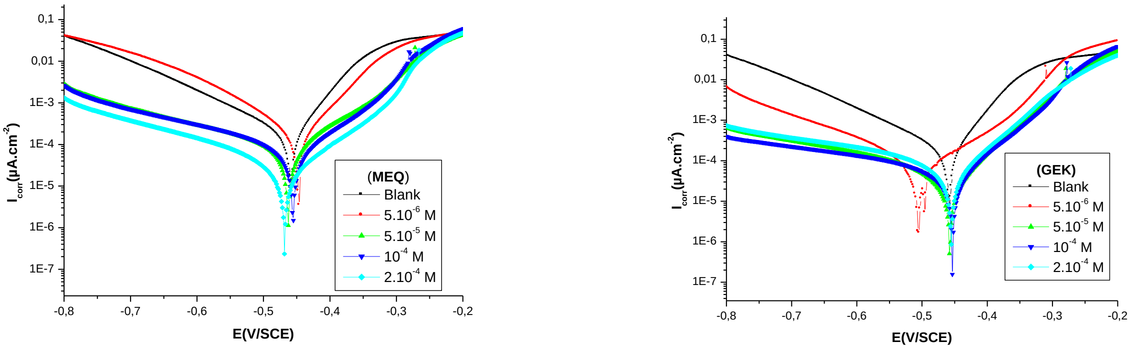


Figure 2: Polarization curves of iron in 1M HCl in absence and presence of different concentrations of: **(**MEQ) and(GEQ)

From this figure, it is noted that the addition of MEQ and GEQ leads to a decrease in the cathodic current densities. This decrease is more pronounced in the case of GEQ. The anodic polarization curves show a decrease in the current densities between E_{corr} and -250 mV/SCE. It seems that at overvoltage higher than -200 mV/SCE, the presence of the surfactants studied does not change the current densities. This phenomenon can be explained by desorption of molecules of ester quats adsorbed to the electrode surface. The parallelcathodicTafelcurvesindicate that the hydrogen evolutionreactionwas activation controlled. The identicalTafelslopesmaysuggestthat the addition of the inhibitorsdoes not modify the proton reductionmechanism. The current densities in absence and presence of different concentrations of the ester-quats were used to determine the protection efficiency according to the following equation:

$$E\% = \left(\frac{i_{cor\ 1} - i_{cor\ 2}}{i_{cor\ 1}}\right) x100 \qquad (1)$$

Where i_{cor1} and i_{corr2} are the corrosion current densities in the absence and presence of inhibitor, respectively, determined by extrapolation of Tafel lines to the corrosion potential.

The electrochemical parameters of iron in presence of both inhibitors are listed in Table 1. These include the free corrosion potential, E_{cor}, corrosion current density, i_{cor}, cathodicTafel slope, B_c, anodic Tafel slope, B_a and protection efficiency, I*E*%.According to Riggs and others [49], if the displacement in E_{corr} is higher than 85 mV with respect to E_{corr}, the inhibitor can be seen as a cathodic or anodic type. In our study, the maximum displacement was 30 mV, which indicates that the inhibitors are mixed-type. The slopes of the cathodicTafel lines in presence of the inhibitorsare comparable with that of the blank. It indicates that the mechanism of the cathodic reaction does not change in presence of the inhibitor and the inhibition action is by simple blocking of the metal surface. From Table1, it can be observed that the current densityvalues decrease when the concentration of (GEQ) and (MEQ)increase. We note also that the decrease of the current density is more pronounced in the case of (GEQ). The inhibition efficiency of GEQ at 2.10^{-4}M reaches 96% against 87%for MEQ in acidic media.

Table 1:Corrosion parameters obtained from Tafel Polarization for iron in 1M HCl with and without addition of different concentrations of MEQand GEQ.

	C (molL^{-1})	**E$_{corr}$ (mV/SCE)**	**I$_{corr}$ (µAcm^{-2})**	**b$_a$ (mVdec^{-1})**	**-b$_c$ (mV dec^{-1})**	**IE (%)**
Blank		-459.3	192	62.6	134.7	-
Mono ester-quat	$5x10^{-6}$	-449.3	128	65.8	140.4	33
MEQ	$5x10^{-5}$	-445.3	113	86.6	146.4	58
	$1x10^{-4}$	-468.2	42	87.3	137.1	78
	$2x10^{-4}$	-483.0	24	97.5	131.1	87
Gemini ester-quat	$5x10^{-6}$	-506.9	82	142.0	144.4	57
	$5x10^{-5}$	-456.0	24	82.3	202.9	87
GEQ	$1x10^{-4}$	-460.0	9	75.2	147.0	95
	$2x10^{-4}$	-468.0	8	72.1	160.0	96

3.2 Electrochemical impedance spectroscopy measurements (EIS)

To confirm the protection ability of the synthesized ester-quat surfactants, electrochemical impedance spectroscopy measurements were performed.

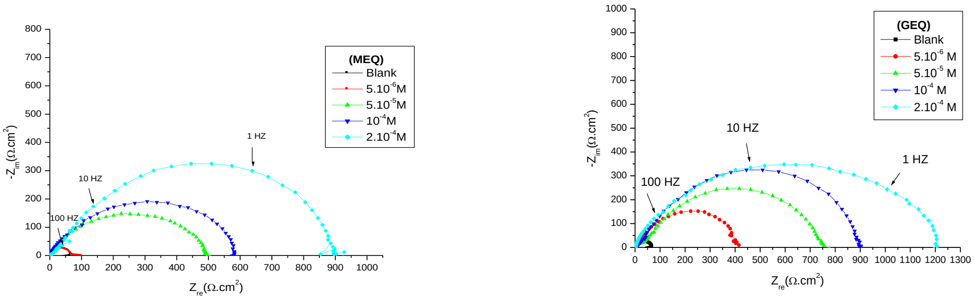


Figure 3: Nyquist diagrams of iron in 1M HCl without and with addition of different concentration of: (MEQ) and (GEQ)

Figure 3 shows the impedance responses of iron in absence and presence of ester-quats surfactants. The impedance parameters calculated from these plots are given in Table 2. The Nyquist plots exhibit one capacitive loop in the absence and presence of inhibitors suggesting that corrosion of iron was charge transfer controlled [50]. The diameter of the capacitive loops increases with increasing concentrations of inhibitors, which suggests that all two compounds act as effective corrosion inhibitors for iron and show the following order of inhibition GEQ>MEQ.The increased diameter of the Nyquist plots in the presence of ester-quats surfactants suggested also that values of charged transfer resistance (R_{ct}) increase due to formation of protective film[51-53]. The recorded EIS data using the electrical circuit of Figure 4 are listed in Table 2. The impedance of the CPE is expressed as follows[54]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} (2)$$

Where Q is the constant phase element (CPE), n is the phase shift which can be explained as a degree of surface inhomogeneity, j is the imaginary unit and ω is the angular frequency. For (n=0),Q represents a resistance; (n=1) a capacitance; (n=-1) an inductance; and for (n=0.5) Warburg impedance.

The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Q and n using the expression [55]:

$$C_{dl} = ({R_{ct}}^{1-n} * Q)^{\frac{1}{n}} (3)$$

The R_{ct} values were used to calculate the inhibition efficiency, IE(%), (listed in Table 2), using the following equation:

$$IE\% = \frac{R^i_{ct} - R^{\circ}_{ct}}{R^i_{ct}} * 100 \qquad (4)$$

Where R^i_{ct} and R°_{ct} are the charge transfer resistance in presence and in absence of inhibitor, respectively.

Table 2: Electrochemical impedance parameters of iron in 1M HCl in the absence and presence of different concentrations of ester-quatinhibitors

	C (mol/L)	R_{ct} ($\Omega.cm^2$)	n	$Q*10^{-4}$ ($S^n.\Omega^{-1}.cm^{-2}$)	C_{dl} ($\mu F.cm^{-2}$)	**IE** (%)
Blank		63.5	0.87	1.901	95.31	-
MEQ	$5x10^{-6}$	80,30	0.82	1.850	73.40	20
	$5x10^{-5}$	422.63	0.78	1.521	70.01	84
	10^{-4}	570.56	0.80	0.828	66.6	88
	2.10^{-4}	920	0.8	0.801	42.3	92
GEQ	$5x10^{-6}$	410.1	0.81	1.183	99.7	85
	$5x10^{-5}$	695.5	0.81	1.115	61.2	91
	10^{-4}	959	0.79	1.111	57.3	93
	2.10^{-4}	1202	0.82	0.325	26.4	95

Inspection of Table 2 reveals that values of R_{ct} increase with increasing ester-quats surfactants concentration suggesting that an increase of efficacity IE% with inhibitor concentration. The values of C_{dl} decreased (Table2) with addition of ester-quats surfactants. This phenomenon is probably due to the decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the ester-quats surfactants strongly adsorbed onto the iron surface [50,52,56]. However for each concentration of inhibitors, higher values of R_{ct} and lower values of double layer capacitance were obtained for the GEQ comparatively to those obtained for MEQ. We deduced that the GEQinhibitory power is better than that of MEQ. These results are in good agreement with those found by polarization curves method.

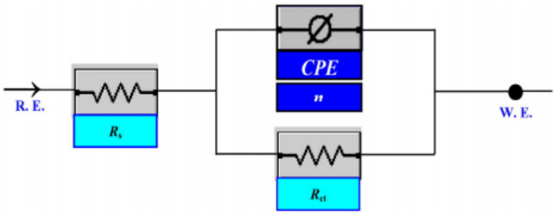
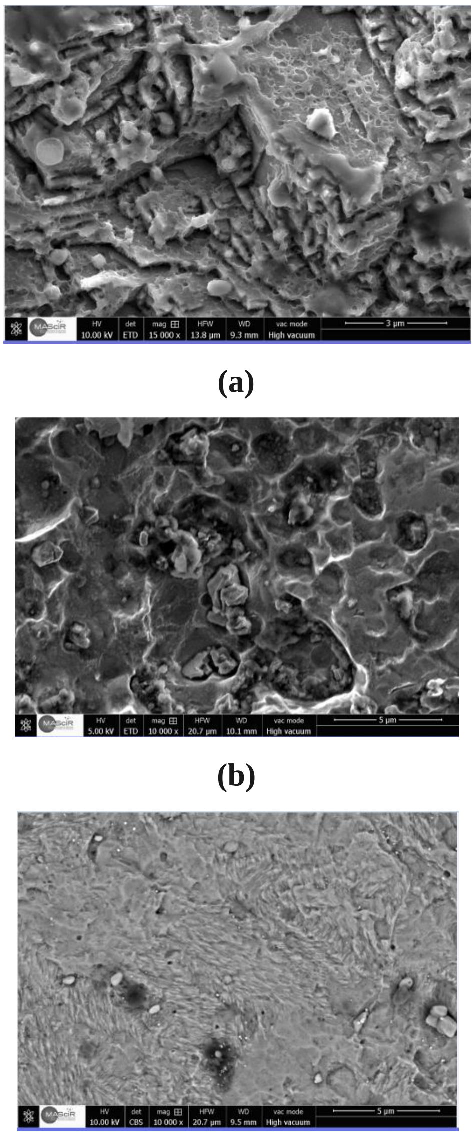


Figure 4: Equivalent circuit model used to fit the impedance spectra.

3.3 Surface characterization (SEM)

SEM micrographs of iron samples after immersion into 1M HCl acid solution in the absence and presence of ester-quat inhibitors are shown in Figure 5 (a, b and c). We note that in the absence of inhibitors, the iron surface is largely roughened and severely damagedby the corrosive environment due to the dissolution of the metal (figure 5 a). Whereas in the presence of ester-quats studied (figure 5 b and c), the corrosion was reduced and a porous white deposit formation is observed. This fact may be due to the adsorption of inhibitor molecules on the iron surface which form a passive film that blocks the active sites. However, it is clear that the iron surface in the presence of GEQ is completely covered with a homogeneous and thicker layer than that observed in the case of MEQ. This can be explained by the strong adsorption of molecules of GEQ on the metal surface. So we can deduce that the GEQ inhibitor protects better the metal surface and therefore it has an inhibitory effect higher than that of MEQ surfactant.



(a)

(b)

(c)

Figure 5: SEM micrographs of iron surfaces **(a)** blank 1M HCl, **(b)** with (MEQ) and **(c)** with (GEQ).

3.4 Adsorption mechanism

A better understanding of the relationship between the adsorption of surfactant molecules onto metal surface and corrosion inhibition is great importance for both theoretical and experimental reasons.Adsorption of the surfactant molecules is found to be responsible for the corrosion inhibition of metal and in general directly related to its capability to aggegate to form micelles [57-59]. The adsorption is described by two main types of interaction namely physical adsorption and chemisorption. It depends on the load of the metal and its nature, the chemical structure of organic product and the type of electrolyte [60-62]. The adsorption of ester-quat inhibitors at the iron/solution interface cannot be simply consider as an electrostatic adsorption, the chemisorptions of the ester function on iron surface must be considered at the same time [63]. The surfactants inhibitors MEQ and GEQ exert their inhibition action by adsorption of the hydrophilic part on the iron surface through the quaternary ammonium cation and ester function. While the hydrophobic part extends to solution face to form a hydrophobic barrier to decrease the corrosion rate. It is well known that the iron surface is positively charged in acidic environments [64]. Therefore, it is difficult for a cationic inhibitor to adsorb on the metal surface positively charged due to the electrostatic repulsion. Halide ions Cl^- and Br^- present in the solution are adsorbed on the iron surface and create an excess of negative charge, which promotes the adsorption of the quaternary ammonium ion of two studied cationic inhibitors. In other words, there may be a synergism between the quaternary ammonium ions and halide ions, which improves the inhibitory ability of the inhibitor [65]. It is accepted that the chemical adsorption process involves a transfer or sharing of electrons between molecules of the inhibitor and orbital « d » of the unsaturated metal surface to form, respectively, coordination bonds or covalent bonds. Electron transfer is done with the orbitals of organic molecules with weakly bound electrons as those having multiple bonds. The transfer is reinforced by the presence of hetero atoms with free electron pairs [66-68].The adsorption mode proposed for the hydrophilic part of the surfactants studied is shown in figure 6.

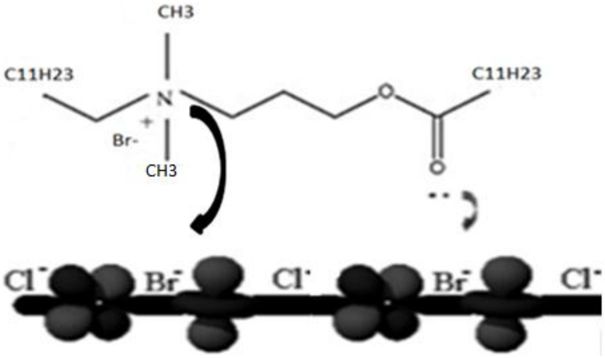


Figure 6: the scheme for ester-quat hydrophilic part adsorbing on iron surface

According to the preceding studies [35-37], the values of standard free energies of adsorption calculated for two esterquats are indicative of chemisorptions and physisorption. The molecule of GEQ has two ester functional groups and two quaternary ammonium cations while the MEQ has only one ester group and a quaternary ammonium cation. This indicates that the adsoption of GEQ is greater than that of MEQ, and therefore greater inhibitory efficiency.

3.5 Quantum chemical study

The researchers are often encouraged to use theoretical data in their studies not only to suport their experimental results but also to find the efficient way to minimize the chemical expenditures. To study the relationship between the molecular structure ofthe surfactants inhibitors and their effeciency, the quantum theoretical calculation method HF with basis sets:HF/STO-3G(d) and HF/6-31 G(d) was used. Density Functional Theory (DFT) is certainly the most widely used methodology for the prediction of chemical reactivity of molecules. DFT /STO-3G* which gives more accurate results in terms of the determination of electronic properties was also investigated. Frontier orbital (HOMO and LUMO) theory is useful in the prediction of adsorption centers and corrosion inhibition of surfactant molecules on the iron surface [69-73]. The molecular structures of studied surfactants and their frontier molecular orbital density distributions (HOMO and LUMO) calculated by Hartree-Fock method are shown in figure 7. The calculated quantum chemical parameters related to the inhibition efficiency of the surfactants such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ($\Delta E = E_{LUMO} – E_{HOMO}$), dipole moment ($\mu$), ionization potential (I), affinity (A), absolute softness (σ), absolute hardness (η),electronegativity (χ) and fraction of transferred electrons(ΔN) are given in Table 3. According to DFT-Koopman's theorem [74-75], E_{HOMO} and E_{LUMO} are related to I and A, respectively, according to the following equations:

$$I = -E_{HOMO} \quad (5)$$
$$A = -E_{LUMO} \quad (6)$$

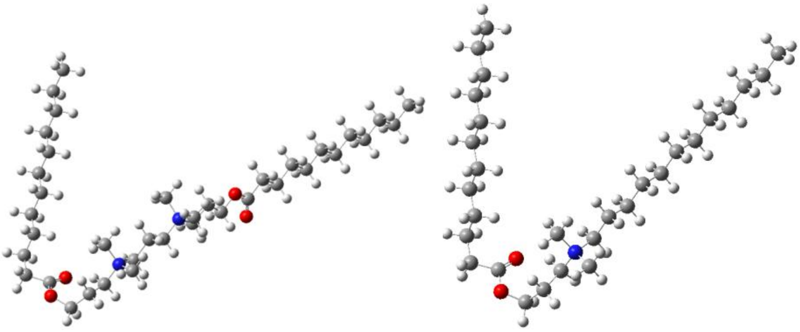
The values of χ and η for inhibitor molecules were determined based on finite difference approximation, as linear combinations of the calculated I and A [76]:

$$\chi = \frac{I+A}{2} \quad (7)$$

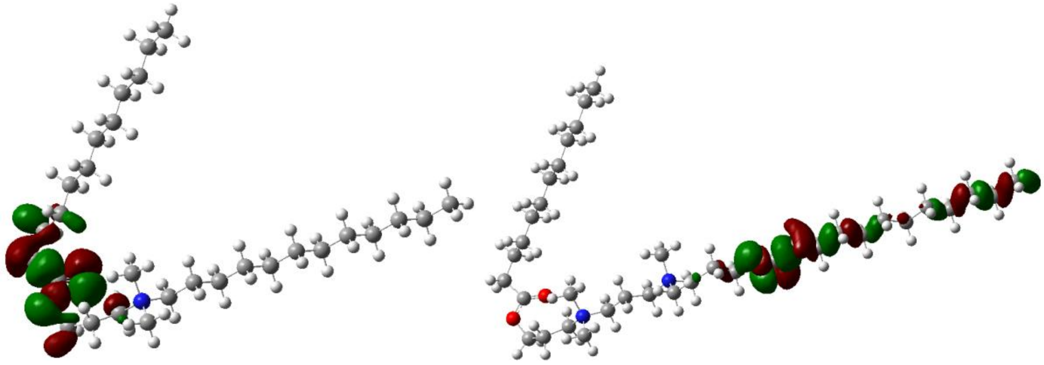
$$\eta = \frac{I-A}{2} \quad (8)$$

Softness parameter is estimated using the following equation [77]:

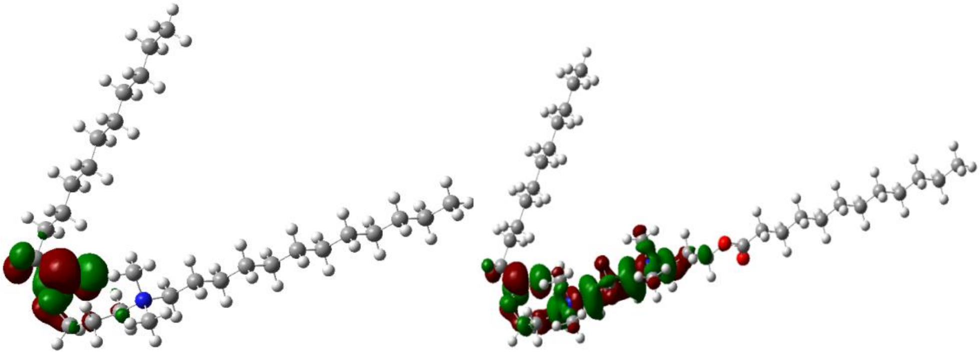
$$\sigma = 1/\eta \qquad (9)$$



Structure (MEQ) Structure (GEQ)



HOMO -1 (MEQ) HOMO -2 (MEQ)



LUMO (MEQ) LUMO (GEQ)

Figure 7: Molecular structures and frontier molecular orbitals of MEQ and GEQ.

The inhibition efficiency of the inhibitor usually depends on the molecules adsorption on the metal surface. In the defining of chemical reactivity or stability of molecules, the energies of highest occupied molecular orbital and lowest unoccupied molecular orbital are important tools. It is well known that the adsorption of the inhibitor to the metal surface increases with an increasing HOMO energy (E_{HOMO}) and a decreasing LUMO energy (E_{LUMO}). According the frontier molecular orbital theory, E_{HOMO} and E_{LUMO} are associated with electron-donating ability and electron accepting ability of a molecule, respectively. A molecule with higher E_{HOMO} value is more capable of giving electrons to an acceptor having appropriate vacant molecular orbitals. On the other hand, lower value of E_{LUMO}indicates greater ability the molecule to accept electron from the filled metal orbitals [78-79].

Table 3:Quantum parameters of studied inhibitors

	Mono ester-quat **MEQ**			Gemini ester-quat **GEQ**		
	HF/STO-3G(d)	HF/6-31 G(d)	B3LYP/STO-3G*	HF/STO-3G(d)	HF/6-31 G(d)	DFT/B3LYP/STO-3G*
E_{HOMO} (eV)	-11.614	-12.7798	-7.095	-11.875	-13.276	-8.321
E_{LUMO} (eV)	5.201	1.271	-0.168	3.239	-1.554	-3.222
ΔE (eV)	16.815	14.034	6.927	15.114	11.722	5.099
μ (D)	19.090	10.2058	10.5336	42.170	35.3767	36.0462
I (eV)	11.614	12.779	7.0950	11.875	13.276	8.321
A (eV)	-5.201	-1.271	0.167	-3.239	1.554	3.222
χ (eV)	3.206	5.769	3.631	4,318	7.347	5.771
η (eV)	8.407	7.025	3.464	7.557	5.861	2.549
σ (eV^{-1})	0.119	0.142	0.288	0.132	0.170	0.392
ΔN	0.226	0.087	0.486	0.177	-0.029	0.241

The results listed in Table 3 show that the highest E_{HOMO} is obtained for MEQ, this result are not sufficient to conclude that MEQ is more efficient than GEQ. Therefore, the high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low empty molecular orbitals [80]. Indeed, the excellent corrosion inhibitors are usually the organic compounds which not only give electrons to the unoccupied orbital of metal, but also to accept free electrons from it [81].The values of highest occupied orbital molecular energies E_{HOMO} are negative, which has been explained by some authors to be an indication of physisorption rather than chemisorptions [82-83].According to the calculated values of the E_{LUMO}, it can be deduced that the GEC is the best inhibitor. This is in good agreement with experimental results.

The difference between E_{HOMO} and E_{LUMO}, referred as the energy gap (ΔE) is an important factor that determines the reactivity of the inhibitor molecule toward the adsorption on the metallic surface [84]. The good corrosion inhibitors have low energy gap values, this is due to that ionization energy required to remove an electron from the last occupied orbital will be low [85]. From the results presented in Table 3 we can conclude that inhibitor GEQ has the lowest energy gap and, hence, the molecule could have better performance as corrosion inhibitor. The theoretical order for the variation of inhibition efficiencies of the studied inhibitors agrees with the experimental data and it is as follows: GEQ > MEQ.

The parameters such as global hardness (η) and softness (σ) are associated with the reactivity and selectivity of the molecule. According to the Lewis theory of acid/bases and also Pearson's hard/soft acids and bases [86], hard molecules would have large ΔE values and would be less reactive, and soft molecule would have smaller ΔE and it would be more reactive. The inhibitor with the highest value of global softness, is expected to have the highest inhibition efficiency [87]. The lower hardness values obtained in the case of the surfactant GEQ show that it has a greater tendency to give electrons to iron. Consequently, the inhibitory capacity of the inhibitors studied is in the order GEQ> MEQ, which is in agreement with the data obtained experimentally.

The dipole moment (μ) indicates the polarity of a covalent bond, which is related to the degree of deviation of electrons. That μ value employed as a predictor for inhibition effectivenes is questioned. Some authors showed that an increase of the dipole moment leads to decrease of inhibition [88-90]. In contrast, the increase of the dipole moment can lead to increase of inhibition [91-92], which could be related to the dipole – dipole interaction of molecules and metal surface. The higher value of μ obtained for GEQ is coherent with the second explanation indicating stronger dipole - dipole interactions of GEQ molecules and metallic surface in comparison to that of MEQ.

The reaserch studies of Bereket and al. [93] showed that excellent corrosion inhibitors are usually organic compounds, which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal.The electronegativity (χ) demonstrate electron attracting ability of the inhibitor molecule.The Higher values of χ indicate strong attracting power to accept electron from the iron surface. Subsequently, the inhibitor molecules which have higher electronegativity would possess higher inhibition efficiency. The values inserted in the table 3 show that the GEQ surfactant electronegativity is higher than the MEQ, which allows that the GEQ inhibitor is more effective than the MEQ.

The fraction of electrons transferred (ΔN)from inhibitor to surface of metal can be calculate using Pearson's method [94], by the following expression:

$$\Delta N = \frac{\chi_{Fe} - \chi_{Surf}}{2(\eta_{Fe} + \eta_{Surf})} \qquad (10)$$

Consequently, to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk iron was used $\chi_{Fe} = 7.0$ eV and a global hardness of $\eta_{Fe} = 0$ eV, respecvely, by assuming that for a metallic bulk I = A because they are softer than the neutral metallic atoms [95-97]. The ΔN values display the electron transfer from iron-surface to molecule if $\Delta N < 0$ and molecule to iron-surface if $\Delta N > 0$ [98]. According to Lukovits and alstudies [99], the inhibition efficiency increases with increasing electron donating capacity to the metal surface when $\Delta N < 3.6$.The values of ΔN calculated according the used methods were insered in table 3.The results show that the MEQ have the highest value of ΔN. Therefore, the highest inhibition efficiency obtained experimentally for GEQ can be explained by the tendency of molecule to receive the electrons. This ability to receive the electron from the metallic surface increases the inhibition efficiency.

Conclusions

Evaluation of the results of electrochemical techniques, surface characterization and quantum chemical calculations led to the following conclusions:

- Results obtained from the polarization curves and the EIS show that the studied surfactants are good inhibitors of iron in 1 M HCl. Both surfactants act as mixed inhibitors. However, we noted that the gemini ester-quat is the most efficient for the corrosion inhibition.
- SEM results show that the inhibition effect is more pronounced in the presence of the gemini ester-quat(GEQ) thanin the presence of mono ester-quat (MEQ).
- The quantum chemical parameters values revealed that the adsorption mechanism of these inhibitors on iron surface in 1M HCL solution is mainly due to chemical and physical adsorption.
- Quantum chemical study shows a good correlation with the results obtained experimentally.

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