ISSN : 0974 - 7486 Volume 9 Issue 9

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(9), 2013 [336-345]

The inhibitive effect and some quantum chemical parameters of cationic surfactants on the corrosion of carbon steel in 1M HCl

O.H.Abdelraheem*, M.I.Nessim, M.M.Osman

Analysis and Evaluation Department, Egyptian Petroleum Research institute (EPRI), 1, Ahmed El- Zomor St.,
Nasr City 11727 Cairo, (EGYPT)
E-mail: omnia_hassan55@yahoo.com

ABSTRACT

The inhibitive effect of two cationic gemini surfactants, with different spacer lengths (12-2-12, 12-5-12), and their conventional form (DOTAB) on carbon steel corrosion in 1 M HCl solution was studied. The chemical structures of synthesized surfactants were characterized by the methodologies ^{1}H-NMR, elemental analysis and XRD. Corrosion inhibition efficiency was investigated by weight loss and Potentiodynamic polarization techniques. The studied surfactants showed good inhibitive characteristics. The obtained data elucidated that the efficiencies vary with concentration, and increases in the following order: 12-2-12 >12-5-12 > DOTAB. Adsorption of the tested surfactants on carbon steel surface in the acid medium obeyed Langmuir isotherm. Adsorption isotherm parameters (K_{ads}, ΔG_{ads}) were determined. The morphology of carbon steel surfaces was examined by scanning electron microscopy (SEM). Quantum chemical calculations were further applied to reveal the molecular structure and explain its effect on the inhibition efficiency. The molecule structural parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, energy gap (E_{HOMO}-E_{LUMO}), the dipole moment and charge densities were calculated.

KEYWORDS

Gemini surfactants;
Surfactant spacer;
Corrosion inhibition;
Carbon steel;
Quantum chemical parameters.

INTRODUCTION

The study of corrosion of steel in acid solutions is industrially important field of research[1-3]. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media[4-6]. Among efficient corrosion inhibitors, there are heterocyclic organic compounds consisting of π-system and/or O, N, P, or S heteroatoms[7]. Recently, the new generation of surfactants so called gemini surfactants has been investigated as corrosion inhibitors for acid solutions[8]. The name gemini surfactants was assigned to a group of surfactants contains two hydrophilic groups in the molecule, separated by a rigid or flexible spacer. Given that, gemini surfactants show many unique properties in comparison with single chain conventional surfactants, it is reasonable to study their effects on corrosion inhibition of metals[9,10]. This work describes corrosion inhibition of carbon steel in 1M HCl by cationic gemini surfactants (designated as 12-5-12, 12-2-12) and their conventional form (DOTAB). Potentiodynamic polarization and mass loss measurement methods were applied to study these cationic gemini surfactants as inhibitors for carbon steel corrosion surface. Scanning Electron Microscope (SEM) investigation was performed, to examine carbon steel surfaces.

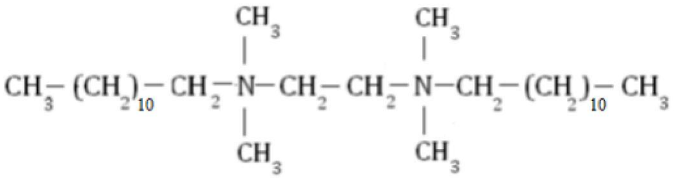
Advances in computer hardware and software and in theoretical chemistry have brought high performance computing and graphic tools within the reach of many academic and industrial laboratories. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity. Recently, more corrosion publications contain substantial quantum chemical calculations. Such calculations are usually used to explore the relationship between the inhibitor molecular properties and their corrosion inhibition efficiencies. The aim of this paper is to extend our investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies of the inhibitors by determining the quantum chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference ΔE (E_{HOMO}-E_{LUMO}), dipole moment (μ (, the Mulliken and Huckel charges data of the inhibitors used[11].

MATERIALS AND METHODS

Synthesis of cationic gemini surfactants

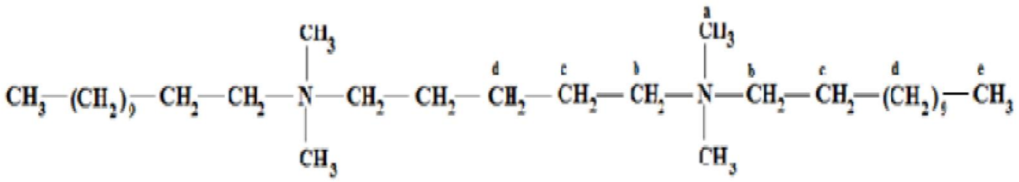
Gemini surfactant (12-2-12), N-dodecanediyl-1,2-ethane bis (dimethyl ammonium bromide) is prepared from N,N,N',N'-tetramethylethylenediamine and dodecyl bromide in absolute ethanol under reflux for 24 hrs using an excess of bromide (25%). After rotary evaporation of the ethanol, a waxy product was obtained. The excess of alkyl bromide was removed by extraction with a mixture of ether-benzene and finally by an extraction with hexane. The resulting product was recrystallized in pure acetone and acetone-ethanol mixtures[12]. The structure is confirmed previously[10].

The second gemini surfactant (12-5-12), N^1,N^5-didodecyl-N^1,N^1,N^5,N^5 thetramethylpentane-1,5-diaminium bromide is prepared from N,N-dimethyl dodecyl amine (0.02 mole) and 1,5-dibromopentane (0.01 mole). The method used is reported previously[12]. The chemical structure of the synthesized compounds was characterized by elemental analysis, ^{1}H-NMR and XRD.



$$CH_3-(CH_2)_{10}-CH_2-\underset{CH_3}{\overset{CH_3}{N}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}-CH_2-(CH_2)_{10}-CH_3$$

N-dodecanediyl-1,2-ethane bis(dimethyl ammonium bromide (12-2-12)



$$CH_3-(CH_2)_9-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N}}-CH_2-CH_2-\overset{d}{CH_2}-\overset{c}{CH_2}-\overset{b}{CH_2}-\underset{CH_3}{\overset{\overset{a}{CH_3}}{N}}-\overset{b}{CH_2}-\overset{c}{CH_2}-\overset{d}{(CH_2)_9}-\overset{e}{CH_3}$$

N^1,N^5-didodecyl-N^1,N^1,N^5,N^5 thetramethylpentane-1,5-diaminium bromide (12-5-12)

Figure 1 : The chemical structure of the prepared cationic gemini surfactants (12-2-12 and 12-5-12).

Weight loss measurements

Different concentration solutions of surfactants in acid medium (1M HCl) were prepared in range from 5 to1000 ppm by using 37% HCl and bi-distilled water. The metal substrate is carbon steel of the following chemical composition: 0.28%C, 1.25%Mn, 0.04%P, 0.05%S, and the balance is Fe. Specimens used in the mass loss measurements are rectangular with 2.5 cm×2.0 cm×0.5 cm dimensions, polished with SiC emery papers up to 1200 grit, washed with bi distilled water, degreased in acetone and dried. The samples were allowed to stand for 24 h in 1M HCl solution in

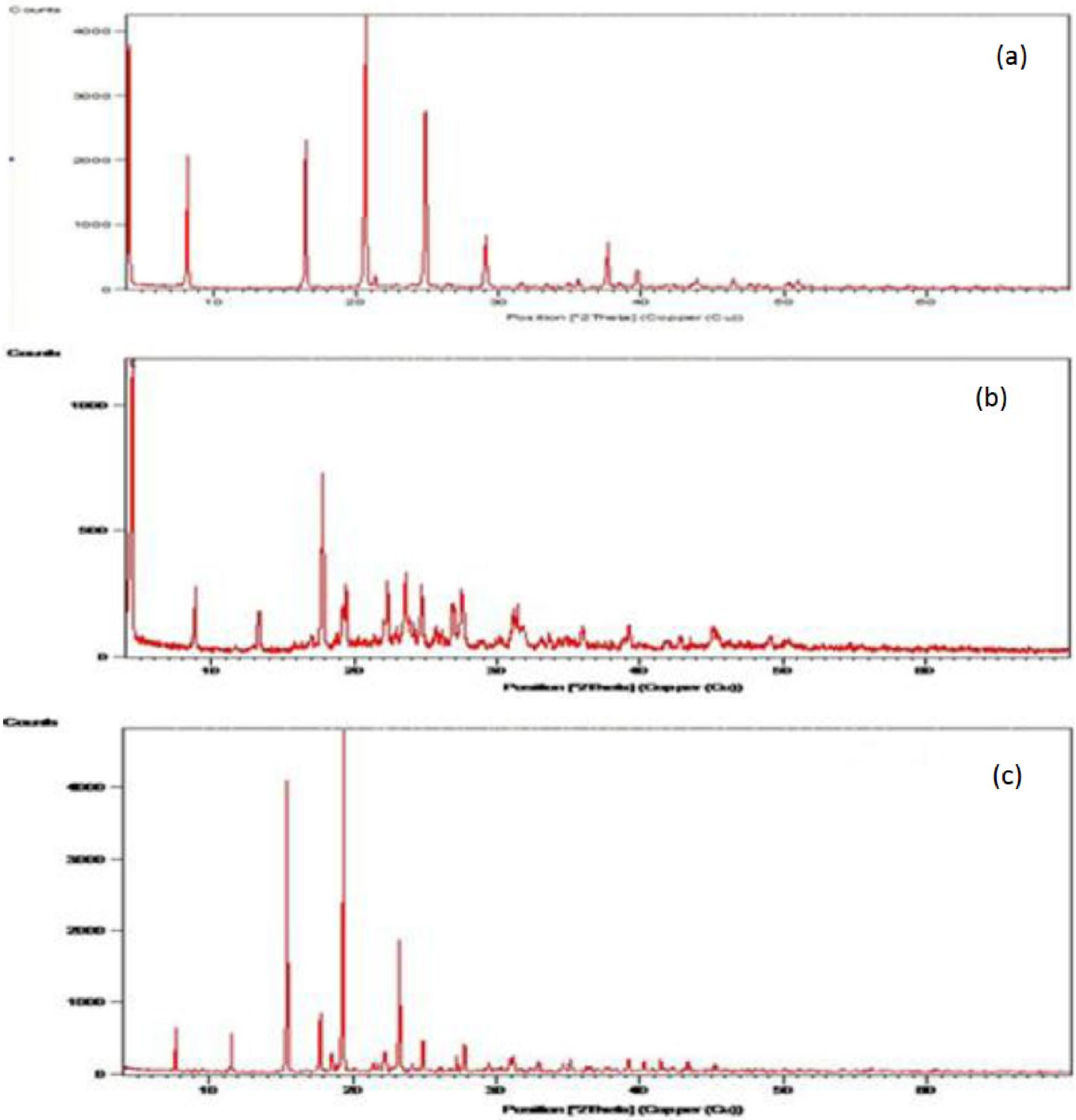


Figure 2 : X-ray diffraction powder analysis (XRD) patterns of the cationic surfactants: (a) DOTAB, (b) 12-2-12 and (c) 12-5-12.

trode was sealed by alardite resin with exposure surface 1.0 cm^2. The experiments were carried out using Potentiostat type Voltalab 40 PGZ 301, with voltamaster 4 software at scan rate 0.5 mV.s^{-1} and at room temperature.

SEM examination

The surface examination of carbon steel samples immersed in 1 M HCl, without and with 400 ppm of tested cationic surfactants was performed using scanning electron microscope (JEOL 5400). The energy of the acceleration beam employed was 30 kv.

Quantum chemical calculations

Quantum mechanical program namely Chem Bio Draw Ultra 12[13], was used for molecular modeling.

The calculations were based on Ab initio and semiemperical (MNDO, AM1 and PM3) methods.

RESULTS AND DISCUSSION

Confirmation of chemical structure of cationic gemini surfactants

The chemical structure of the cationic gemini surfactants was confirmed by elemental analysis, ^{1}HNMR and XRD.

(a) Elemental analysis

Elemental analysis was performed for the prepared surfactant (12-5-12) via Elemental Analyzer Perkin Elmer 240 C, and the obtained results are given in TABLE 1.

TABLE 1 : The calculated and founded percentage values of C, H, and N for 12-5-12.

Elements	%C		%H		%N	
	Calculated	Found	Calculated	Found	Calculated	Found
12-5-12	57.72	57.54	10.50	10.79	4.08	4.14

(b) ^{1}H-NMR

In the present work (12-5-12) was investigated using Jeol-EX-270 MHz ^{1}H-NMR Spectrophotometer. The following bands were shown (MHz, δ, CDC13/ TMS): (a) s, 3.32 ppm; (b) t, 2.26 ppm; (c) m, 1.72 ppm; (d) m, 1.30 ppm; (e) m, 0.84 ppm.

(c) X-ray diffraction analysis (XRD)

Figure 2 shows X-ray diffraction patterns of the three cationic surfactants. Using (ICDD PDF+4 2011) database individual crystalline phases were identified in the samples of surfactants. From their observed XRD patterns, we noticed that the three surfactants presented in crystalline forms.

Weight loss measurements

The loss in weight was determined by analytical balance. The inhibition efficiency (E_W%) was obtained by Eq.1[14]:

$$E_W \% = (W_o - W)/W_o \times 100 \qquad (1)$$

where W_o and W are the weight losses per unit area in the absence and presence of the inhibitors, respectively. Figure 3 shows the variation of the concentration with the inhibition efficiency. While the cationic surfactants were added to the acid solution, it was found that the inhibition efficiency raised till reaches steady-state values. The increase in inhibition efficiency with increasing inhibitor concentration may be attributed to the formation of a barrier film, which prevents the attack of acid on the metal surface[15]. The inhibition efficiencies are in the order: 12-2-12> 12-5-12 > DOTAB.

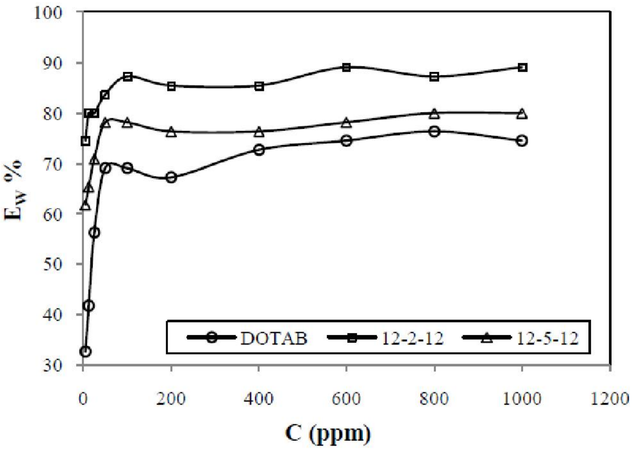


Figure 3 : Variation of the inhibition efficiency of carbon steel in the presence of different concentrations of the inhibitors

Polarization curves

Typical polarization curves of carbon steel in 1M HCl in the presence and absence of inhibitors are shown Figure 4-7. Electrochemical parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βa, βc) and corrosion current density (i_{corr}) obtained from the Tafel extrapolation of the polarization curves, were given in TABLE 2, where the inhibition efficiency (E_p%) was calculated by the following equation[16]:

$$E_p \% = (i^o_{corr} - i_{corr}) / i^o_{corr} \times 100 \quad (2)$$

where $i^o_{corr,}$ and i_{corr} are uninhibited and inhibited corrosion current densities respectively. From tabulated data, It can be observed that the current density i_{orrr} values have a trend to decrease with the increasing inhibitor concentration, correspondingly, inhibition efficiencies (E_p%) values increase with the increasing inhibitor concentration and then reach a maximum value. No definite trend was observed in the shift E_{corr} values in the presence of different concentrations of the cationic inhibitors.

It could be also noticed that anodic currents were suppressed with the increasing concentration, which suggested that the tested surfactants reduced anodic dissolution and behave as anodic type inhibitors.

A comparison between the inhibitory effects of the cationic surfactants under study is illustrated in Figure 7. The results obtained from both weight loss measurements and the polarization measurements were in good agreement and states that gemini cationic surfactants have higher inhibitive effect than that of the monomer DOTAB, and also show that the longer the spacer of the gemini surfactant, the lower its inhibition efficiency in the order: 12-2-12 >12-5-12. This behavior could be attributed to the way that surfactant molecules adsorbed on the metallic substrate depending on the length of the spacer[17]. The same behavior was reported in previous work for zinc corrosion inhibition, where the inhibition efficiency slightly reduced with increasing spacer length[18].

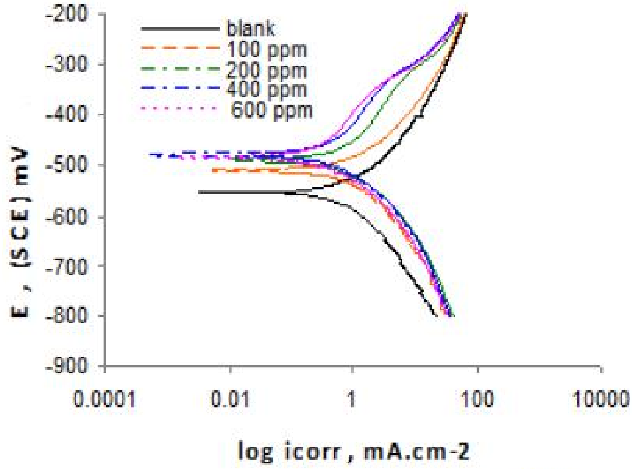


Figure 4 : Potentiodynamic polarization of carbon steel in 1M HCl with different concentrations of DOTAB.

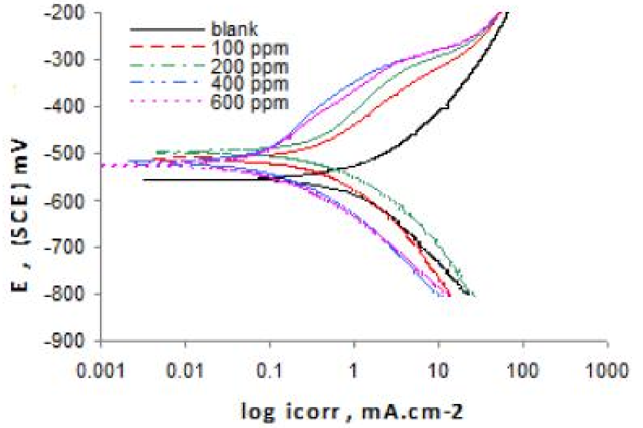


Figure 5 : Potentiodynamic polarization of carbon steel in 1M HCl with different concentrations of the gemini surfactant 12-2-12.

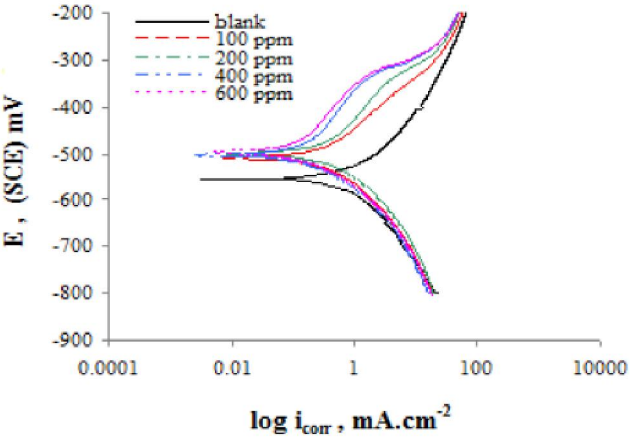


Figure 6 : Potentiodynamic polarization of carbon steel in 1M HCl with different concentrations of the gemini surfactant 12-5-12

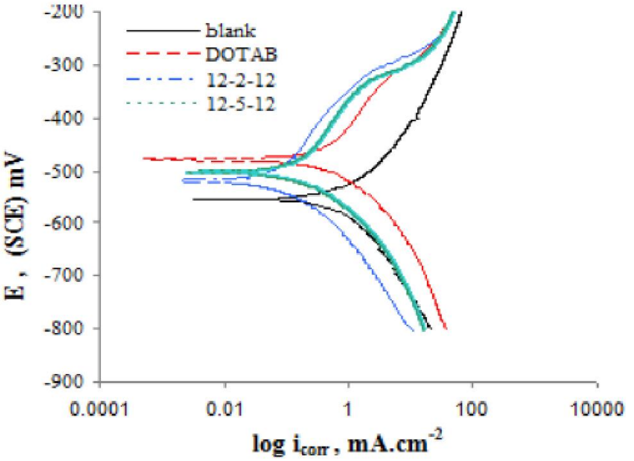


Figure 7 : Potentiodynamic polarization of carbon steel in 1M HCl in absence (blank) and presence of 400ppm from DOTAB, 12-2-12 and 12-5-12.

Adsorption isotherm

To obtain more information about the interaction between the inhibitor molecules and the metallic substrate, adsorption isotherm should be tested. All adsorption isotherms are of the general form as in Eq.3[19]:

$$f(\theta,x)\exp(-2a\,\theta) = K_{ads}\,C \qquad (3)$$

where $f(\theta,x)$ is the configuration factor which depends upon the physical model and the assumption underlying the derivation of the isotherm, θ the surface coverage, C the inhibitor concentration in the bulk of solution, 'a' the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface (this is a measure for the steepness of the adsorption isotherm), K_{ads} is the adsorption-desorption equilibrium constant.

TABLE 2 : Electrochemical parameters for the corrosion of carbon steel in 1 M HCL containing different concentrations of inhibitors at 25°C.

Inhibitor	$C_{inhibt.}$ (ppm)	E_{corr} (mV)	i_{corr} (μA·cm$^{?2}$)	βa (mV·dec$^{?1}$)	βc (mV·dec$^{?1}$)	E_P %
Blank	0.00	-563.8	3.3763	188.4	-227.1	0.00
DOTAB	5.0	-504.8	2.3897	154.4	-192.7	29.22
	10.0	-517.3	2.0411	135.2	-181.1	39.57
	25.0	-444.3	1.3676	118.2	-204.5	59.49
	50.0	-514.2	1.3234	197.0	-214.2	60.80
	100	-514.6	1.2198	280.5	-209.7	63.87
	200	-492.9	1.1933	272.5	-186.2	64.65
	400	-481.6	1.1321	171.6	-168.4	66.49
	600	-470.8	0.7642	274.3	-244.2	77.36
	800	-486.5	0.7610	171.2	-178.0	77.46
	1000	-510.1	0.7746	166.5	-186.9	77.05
12-2-12	5.0	-512.8	1.6324	161.1	-195.4	51.65
	10.0	-504.3	1.1166	121.7	-133.5	66.92
	25.0	-535.9	0.4423	92.40	-169.9	86.89
	50.0	-560.2	0.5754	130.5	-174.3	82.95
	100	-514.8	0.3763	156.0	-138.6	88.85
	200	-499.9	0.3220	173.1	-99.40	90.46
	400	-521.5	0.2489	214.4	-168.2	92.62
	600	-527.4	0.2105	196.8	-149.6	93.76
	800	-521.7	0.1728	173.3	-126.2	94.88
	1000	-521.6	0.1429	156.0	-161.8	95.76
12-5-12	5.0	-520.9	2.0421	165.3	-217.4	39.51
	10.0	-536.0	1.6882	154.2	-193.5	49.99
	25.0	-547.3	1.1489	153.4	-210.5	65.97
	50.0	-510.8	0.6985	128.1	-170.1	79.31
	100	-511.1	0.8565	160.4	-214.1	74.63
	200	-502.9	0.7611	233.7	-169.3	77.45
	400	-505.5	0.7124	241.3	-194.6	78.89
	600	-499.7	0.7027	130.4	-214.0	79.18
	800	-543.8	0.6206	124.0	-144.8	81.62
	1000	-530.6	0.6390	118.7	-145.3	81.07

Attempts were made to fit the degree of surface coverage (θ) for different concentrations of inhibitors in 1 M HCl evaluated from weight loss measurement to various isotherm including Frumkin, Langmuir, Temkin, Dahr Flory-Hugins and Al-Awady isotherm models. In according with previous works, by far the best fit was obtained with the Langmuir isotherm by the following relation[17,20]:

$$C/\theta = C + 1/K_{ads} \qquad (4)$$

TABLE 3. shows the parameters and the regression factor calculated from Langmuir adsorption isotherm. Figure 8 gives the result of Langmuir's plot for corrosion inhibition data of the compounds. These results show that all the linear correlation coefficients (r^2) are almost equal to I and all the slopes are very close to 1, which indicates the adsorption of inhibitor onto steel surface accords with Langmuir adsorption isotherm[20]. The values of K_{ads} were found to be 4.1137 x10^4, 24.981 x10^4 and 16.3059 x10^4 for DOTAB, 12-2-12 and 12-5-12 respectively. The relatively high value of the adsorption equilibrium constant reflects the high adsorptive ability of this compound on the metal surface[21].

The standard free energy of the adsorption, ΔG°_{ads}, is related to the constant of equilibrium constant K_{ads}, with the following equation[22].

$$-\Delta G^\circ_{ads} = RT \ln (55.5\ K_{ads}) \qquad (5)$$

where R is the gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in solution expressed in M. The large negative value of ΔG°_{ads} indicated that inhibitors were strongly adsorbed on the surface[23]. Values of ΔG°_{ads} of the order of 20 kJ mol^{-1} or lower are generally consistent with physisorption. Those of the order of 40 kJ kJ mol^{-1} or higher involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond[20,24]. The free energy of adsorption of DOTAB, 12-2-12 and 12-5-12, were calculated and found to be equal to -36.2743, -40.7432 and -39.6864 kJ.mol^{-1} respectively. Indicating that adsorption mechanism of the investigated surfactants is both physical and chemical adsorption. Higher value of the adsorption constant and more negative free energy of adsorption can be reasoned for better adsorption and higher inhibition efficiency[23], which is consistent with data obtained from electrochemical investigations.

TABLE 3 : Adsorption parameters of inhibitors surfactants on the steel surface at 25 °C.

Surfactant	Linear correlation coefficient, r^2	slope	K_{ads} (l. mol^{-1})	ΔG°_{ads} (kJ.mol^{-1})
DOTAB	0.9987	1.0023	4.1137 x 10^4	-36.2743
12-2-12	0.9996	1.0071	24.981 x 10^4	-40.7432
12-5-12	0.9995	1.0021	16.3059 x 10^4	-39.6864

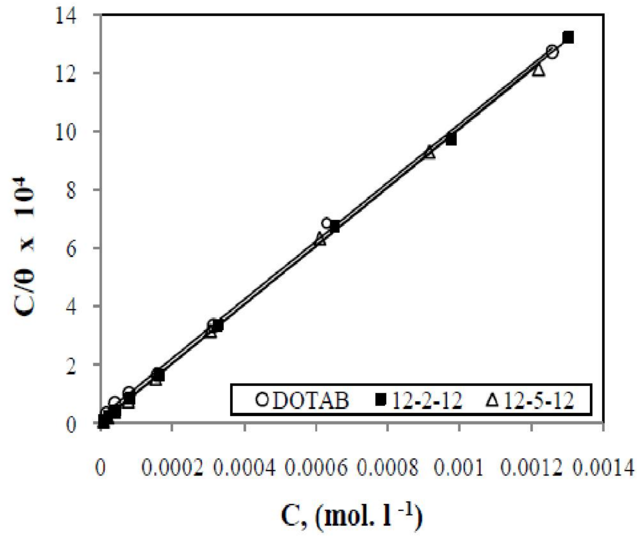


Figure 8 : Langmuir isotherm plots for carbon steel in 1HCl at presence of different concentrations of cationic inhibitors DOTAB, 12-2-12 and 12-5-12.

Quantum chemical calculations

Geometric structures of the cationic surfactants DOTAB, 12-2-12 and 12-5-12 given in Figure 9. The optimized molecular structure of the studied molecules, using Ab initio (HF/3-21G) and semiemperical (MNDO, AM1, MP3) methods, are shown in Figure (10-12). The calculated quantum chemical indices of E_{HOMO}, E_{LUMO}, dipole moment (μ(, ΔE (E_{Lumo}-E_{Homo}), Mulliken and Huckel charges data are given in TABLES 4, 5 and 6.

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species[25]. Thus, the treatment of the frontier molecular orbitals separately from the other orbitals, is based on the general principles governing the nature of chemical reactions. HOMO is often associated with the electron donating ability of a 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[26]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecule would accept electrons. Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low[27], which facilitate adsorption (and therefore inhibition).

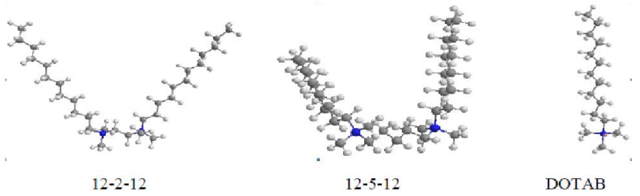


Figure 9 : Optimized structure of the molecules: 12-2-12, 12-5-12 and DOTAB.

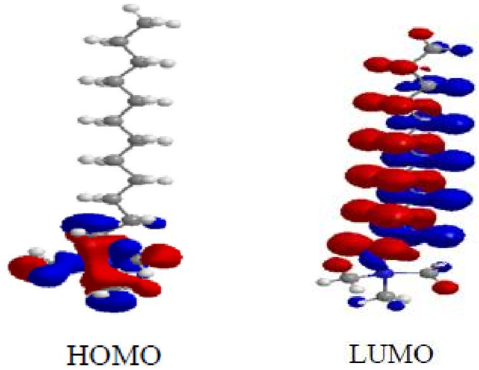


Figure 10 : The frontier molecule orbital density distributions of DOTAB.

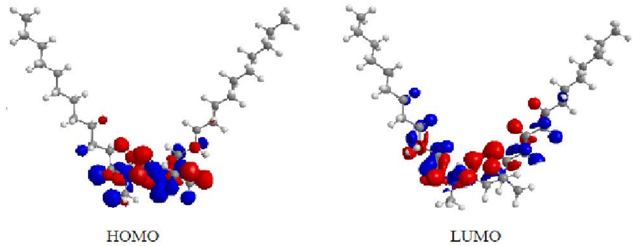


Figure 11 : The frontier molecule orbital density distributions of 12-2-12.

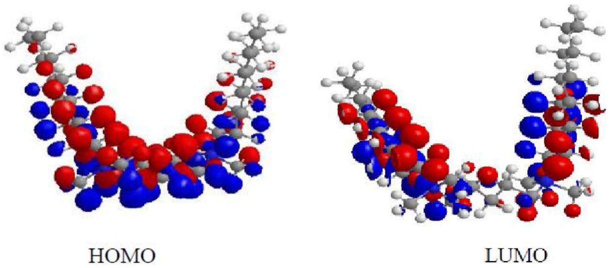


Figure 12 : The frontier molecule orbital density distributions of 12-5-12.

From the given data in TABLES (4-6), it was noted that the higher value of calculated ΔE obtained by DOTAB, while the lower energy gap value was that of 12-2-12. That give good evidence on the obtained efficiency of the studied cationic surfactants to inhibit the corrosion of carbon steel in the hydrochloric acid solutions. Regarding the dipole moment (μ), it can be observed from the present work that the dipole moment increases by decreasing the energy gap.

TABLE 4 : Quantum chemical parameters of DOTAB.

Quantum parameters	HF(3-21G)	PM3	AM1	MNDO	MP2
E_{HOMO} (eV)	27.479	27.471	27.469	27.311	27.476
E_{LUMO} (eV)	28.577	28.564	28.562	28.564	28.571
$E_{LUMO-HOMO}$ (eV)	1.098	1.093	1.093	1.253	1.095
Huckel charge (eV)	N_{13} = 0.7699	N_{13} = 0.7680	N_{13} = 0.7679	N_{13} = 0.7681	N_{13} = 0.7681
Mulliken charge(eV)	N_{13} = -0.7826	N_{13} = 0.6196	N_{13} = -0.0278	N_{13} = -0.1113	N_{13} = -0.7565
μ (Debye)	2.6067	2.0132	2.0241	2.02825	2.6939

TABLE 5 : Quantum chemical parameters of 12-2-12.

Quantum parameters	HF(3-21G)	PM3	AM1	MNDO	MP2
E_{HOMO} (eV)	25.163	26.562	27.217	26.541	26.539
E_{LUMO} (eV)	24.462	27.270	26.514	27.215	27.222
$E_{LUMO-HOMO}$ (eV)	0.701	0.708	0.00697	0.674	0.683
Huckel charge (eV)	N_{13} = 0.68971 N_{18} = 0.73972	N_{13} = 0.75773 N_{18} = 0.76182	N_{13} = 0.75732 N_{18} = 762174	N_{13} = 0.7577 N_{18} = 0.7618	N_{13} = 0.75734 N_{18} = 0.76211
Mulliken charge(eV)	N_{13} = -0.7504 N_{18} = -0.7483	N_{13} = 0.6133 N_{18} = 0.6166	N_{13} = 0.0274 N_{18} = 0.0279	N_{13} = -0.1047 N_{18} = -0.1024	N_{13} = 0.6957 N_{18} = 0.7023
μ (Debye)	4.6169	3.0872	3.0904	3.914	4.0881

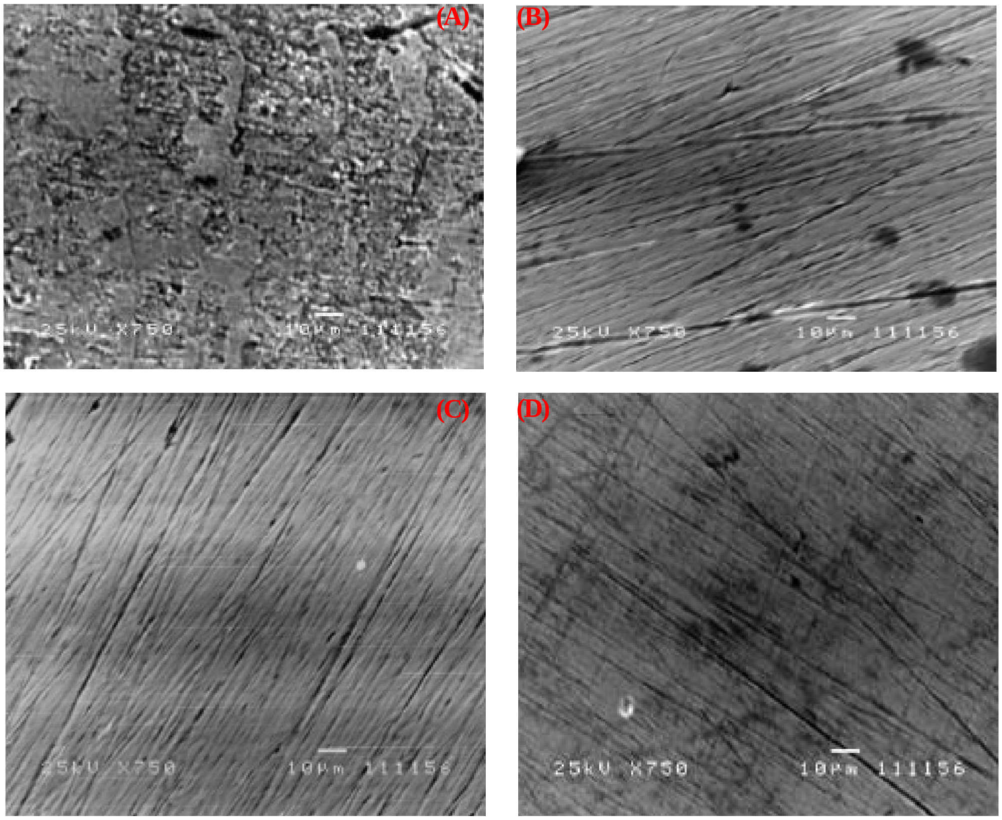


Figure 13 : Scanning electron micrographs of low carbon steel specimens surfaces after immersion for 144 h in1 M HCl in (a) the absence and (b), (c) and (d); presence of surfactants DOTAB, 12-2-12 and 12-5-12 respectively. (Magnification 750 x).

Scanning electron microscopy (SEM)

Figure 13. shows SEM image of carbon steel surface (X 750) after immersion in 1M HCl for 144 hrs in absence of inhibitor (Blank), and after immersion in HCl for the same time interval in presence of 400 ppm of the cationic surfactants DOTAB, 12-2-12, and 12-5-12 respectively. The resulting scanning electron micrographs reveal that the surface was strongly damaged in

TABLE 6 : Quantum chemical parameters of 12-5-12.

Quantum parameters	HF(3-21G)	PM3	AM1	MNDO	MP2
E_{HOMO} (eV)	26.757	26.750	26.111	26.762	26.459
E_{LUMO} (eV)	27.462	27.454	26.816	27.455	26.754
$E_{LUMO-HOMO}$ (eV)	0.707	0.704	0.705	0.693	0.705
Huckel charge (eV)	N_{13} = 0.6711 N_{21} = 0.5820	N_{13} = 0.6272 N_{21} = 0.6021	N_{13} = 0.7097 N_{21} = 0.5659	N_{13} = 0.6698 N_{21} = 0.6045	N_{13} = 0.6110 N_{21} = 0.5617
Mulliken charge(eV)	N_{13} = -0.7584 N_{21} = -0.7565	N_{13} = 0.6165 N_{21} = 0.6141	N_{13} = -0.1022 N_{21} = -0.-1021	N_{13} = -0.1044 N_{21} = -0.1059	N_{13} = -0.7182 N_{21} = -0.7389
μ (Debye)	2.8731	2.2031	2.1325	2.1045	2.6749

absence of the inhibitor, but in presence of optimum concentration of surfactants there is much less damage of the surface. It is clear that, micrograph 12-2-12 shows smooth, well inhibited surface that confirms the good adsorption of 12-2-12 onto the used metal surface and, in turn, a high inhibition efficiency at this concentration.

CONCLUSIONS

The main conclusions of the present work can be reported as following:

(1) The inhibitive effect of two cationic gemini surfactants with different spacer length (12-2-12 and 12-5-12) and their conventional single chained type (DOTAB) on the corrosion behavior of low carbon steel in 1M HCl, was investigated by weight loss and potentiodynamic polarization techniques. The surfactants show good inhibition efficiency and acted as anodic type inhibitors. The inhibition efficiency found to be in the order, 12-2-12>12-5-12>DOTAB.

(2) The adsorption of tested cationic surfactants on the carbon steel obeyed Langmuir adsorption isotherm model.

(3) Quantum chemical calculations were found to give good reasonable correlation with the results obtained by weight loss and potentiodynamic polarization techniques.

REFERENCES

[1] H.K.Sharma, M.A.Quraishi; Indian Journal of Chemistry, **14**, 994 **(2002)**.

[2] M.A.Quraishi, M.A.W.Khan, D.Jamal, M.Ajmal, S.Muralidharan, S.V.K.Iyer; J.Appl.Electrochem, **26**, 1253 **(1996)**.

[3] M.M.Osman, A.M.A.Omar, A.M.Al-Sabagh; Mater.Chem.Phys, **50**, 271 **(1997)**.

[4] L.Qiu, A.Xie, Y.Shen; Materials Chemistry and Physics, **91**, 269 **(2005)**.

[5] E.H.El Ashry, A.El Nemra, S.A.Essawyb, S.Ragab; Progress in Organic Coatings, **61**, 11 **(2008)**.

[6] X.Li, G.Mu; Corrosion Science, **252**, 1254 **(2005)**.

[7] A.Kokalj; Electrochimica Acta, **56**, 745 **(2010)**.

[8] M.El Achouri, M.R.Infante, F.Izquierdo, S.Kertit, H.M.Gouttaya, B.Nciri; Corrosion Science, **43**, 19 **(2001)**.

[9] D.Shukla, V.K.Tyagi; Journal of Oleo Science, **55**, 381 **(2006)**.

[10] I.M.Nessim, A.Hamdy, M.M.Osman, M.N.Shalaby; J.American Science, **7**, 78 **(2011)**.

[11] G.Gece; Corros.Sci., **50**, 2981 **(2008)**.

[12] A.R.Tehrani Bagha, H.Bahrami, B.Movassagh, M.Arami, F.M.Menger; Dyes Pigments, **72**, 331 **(2007)**.

[13] Chem Bio Draw Ultra 12 Software.

[14] M.Abdallah, A.Y.El-Etre; Portugaliae Electrochimica Acta, **21**, 315 **(2003)**.

[15] F.Bensajjay, S.Alehyen, M.El Achouri, S.Kertit; Anti-Corrosion Methods and Materials, **50**, 402 **(2003)**.

[16] H.Ashassi-Sorkhabi, Z.Ghasemi, D.Seifzadeh; Applied Surface Science, **249**, 408 **(2005)**.

[17] L.Qiu, A.Xie, Y.Shen; Applied Surface Science, **246**, 1 **(2005)**.

[18] W.Huang, J.Zhao; Colloids and Surfaces A: Physicochemical and Engineering Aspects, **278**, 246 **(2006)**.

[19] M.A.Amin; J.Appl.Electro.Chem., **36**, 115 **(2006)**.

[20] M.A.Hegazy, M.Abdullah, H.Ahmed; Corrosion Science, **52**, 2897 **(2010)**.

[21] M.A.Migahed, E.M.S.Azzam, A.M.Al-Sabagh; Materials Chemistry and Physics, **85**, 273 **(2004)**.

[22] X.Li, S.Deng, G.Mu, H.Fu, F.Yang; Corrosion Science, **50**, 420 **(2008)**.

[23] A.S.Fouda, A.S.Ellithy; Corros.Sci., **51**, 868

(2009).

[24] L.Larabi, O.Benali, S.M.Mekelleche, Y.Harek; Applied Surface Science, **253**, 1371 **(2006)**.

[25] K.Fukui; Theory of orientation and stereoselection, Springer-Verlag, NewYork, **(1975)**.

[26] T.Arslan, F.Kandemirli, E.E.Ebenso, I.Love, H.Alemu; Corrosion Science, **51**, 35 **(2009)**.

[27] Y.Yana, W.Li, L.Caia, B.Houb; Electrochimica Acta, **53**, 5953 **(2008)**.