Accepted Manuscript

Novel synthesized Schiff Base-based cationic gemini surfactants: Electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion



Hany M. Abd El-Lateef, Kamal A. Soliman, Ahmed H. Tantawy

S0167-7322(16)34104-6
doi: 10.1016/j.molliq.2017.02.105
MOLLIQ 7018
Journal of Molecular Liquids
17 December 2016
23 February 2017
25 February 2017

Please cite this article as: Hany M. Abd El-Lateef, Kamal A. Soliman, Ahmed H. Tantawy , Novel synthesized Schiff Base-based cationic gemini surfactants: Electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Molliq(2017), doi: 10.1016/j.molliq.2017.02.105

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Novel Synthesized Schiff Base-based Cationic Gemini Surfactants: electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion

Hany M. Abd El-Lateef^{a, b}*, Kamal A. Soliman^c, Ahmed H. Tantawy^c ^a Department of Chemistry, College of Science, King Faisal University, Al Hufuf, 31982 Al Hassa, Saudi Arabia ^bChemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt

^c Chemistry Department, Faculty of science, Benha University, 13518Benha, Egypt

* Corresponding author: Fax: (+2)-093 -4601159

Tel: (+2)-012-28-137-103

E-mail address: <u>Hany shubra@yahoo.co.uk</u> (Hany M. Abd El-Lateef)

Novel Synthesized Schiff Base-based Cationic Gemini Surfactants: electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion

<u>Abstract</u>

Three novel Schiff base compounds were synthesized and characterized using spectroscopic methods (FT-IR, ¹H NMR and ¹³C NMR). Their critical micelle concentrations were determined by conductimetric and surface tension measurements. The inhibition potentials of the prepared surfactants on mild steel corrosion in H₂SO₄ have been investigated using electrochemical and scanning electron microscopy techniques. The results showed that all surfactants are good inhibitors for mild steel corrosion with the percentage inhibition efficiency of up to 99.21 % at 1.0 mM. The data showed that the studied surfactants are mixed-type inhibitors. Adsorption of the inhibitors obeyed the Langmuir isotherm. The results obtained from theoretical calculations support our experimental studies.

Keywords: Schiff Base Surfactants; mild steel; EIS; SEM; adsorption; acid inhibition

1. Introduction

Mild steel is a widely used as the constituent materials in various industry fields because of its high mechanical strength and low cost [1-3]. Industrial infrastructures include reactors, drums, petrochemical process devices, boilers, and heat exchangers. In oil and gas industries, aqueous acidic solution (especially hydrochloric and sulphuric acids) is used for acid pickling of steel, de-scaling, acid treatment, chemical improvement and processing or production, and oil well acidification. In this case, the exposure of metal to aqueous acidic solution causes corrosion, which puts safety and economic parts at high risk [3, 4]. Consequently, corrosion inhibitors are used to minimize the rate of corrosion and prohibit the metal from corrosion. This naturally means that it is very important for the workers in the petroleum and related industries to find efficient corrosion inhibitors [5]. The majority of the well-known inhibitors which are effective in acid media there are the organic compounds containing heteroatoms, such as N, O, or S, and/or aromatic rings and/or multiple bonds, which provide a physical or chemical adsorption zone for the metal surface [6-8]. However, most of these compounds are toxic and expensive [9-11]. For this reason, current research activities are being garnered towards the development of cheap, readily available, and "green" corrosion inhibitors with high inhibition efficiency even at much reduced concentrations [12, 13].

Schiff base-based gemini surfactants are considered nontoxic and watersoluble organic compounds [14, 15]. These kinds of compounds have superior surface activity, surface properties and have interesting rheological properties at low concentrations [16-18]. Recent publications revealed that the inhibition efficiency of Schiff bases is much greater than that of corresponding aldehydes and amines in acidic media for different metals such as steel, aluminum and zinc due to the presence

of a –CH=N- group in the molecules **[19-21]**. Schiff bases may also be changed to surfactant and find application as potential inhibitors **[22]**. Gemini surfactants containing imine group and their implementations in corrosion inhibition of metals are rarely reported.

Recently, a quantum chemical calculation is extensively used for correlating the molecular structure of inhibitors and their inhibitive performance and it is also considered a very powerful method to probe the inhibitor/surface interaction and to analyze empirical data [2, 21, 23].

In the present work, the efficiency of three novel Schiff base-based cationic gemini surfactants namely, 53,3 '-(pentane-2,4-diylidenebis(azanylylidene))bis(N-(2-(decyloxy)-2-oxoethyl)-N,N-dimethylpropan-1-aminium) chloride (**SBGS-10**), 3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-oxo-2-

(tetradecyloxy)ethyl)propan-1-aminium) chloride (**SBGS-14**), and 3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-(hexadecyloxy)-2-

oxoethyl)propan-1-aminium) chloride (**SBGS-16**) as biodegradable corrosion inhibitors for mild steel in 1.0 M H_2SO_4 is discussed on the basis of electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) data and scanning electron microscopy (SEM). The critical micelle concentration (CMC) and the surface parameters of the prepared surfactants were determined by surface tension and conductivity measurements. Some quantum chemical indices based theoretical calculations were used to support our experimental investigations.

2. Experimental Section

2.1. Materials

Decyl, tetradecyl and hexadecyl alcohols were obtained from Acros organics company (Belgium). 2-Chloroacetylchloride (97%), Acetylacetone (97%) and 3-(N, N

dimethylamino)-1-propylamine (99%) was purchased from Aldrich company. Diethylether (99%), K_2CO_3 (anhydrous), triethylamine (97%), Dichloromethane (98%), and ethyl alcohol (99%), are high grade and obtained from AL-Nasr chemical company.

2.2. Instruments

The synthesized compounds were elucidated by spectroscopic tools (FTIR, ¹H and ¹³C NMR). The FTIR analysis was done in faculty of science, Benha university using a thermo Nicolet iS10 FTIR spectrophotometer recorded in KBr. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were done in Sohag university using FT-IR-ALPHA-BRUKER-Platinum-ATR measured in DMSO-*d*6.

2.3. Synthesis of Schiff Base cationic Gemini Surfactants (SBGS)

2.3.1. Synthesis of alkyl 2-chloroacetate [compound I]

In 100 mL round-bottom flask, chloroacetyl chloride (3.86 g, 35 mmol) was placed in an ice-water bath with continuous stirring. Decyl, tetradecyl and hexadecyl alcohols separately, triethylamine and dichloromethane (4 g, 35 mmol), (20 mL) were added slowly through 15 min in ice bath. The reaction mixture was remained under stirring for 4 h at 25 $^{\circ}$ C. The solvent was evaporated and separated by rotary evaporator and the product was obtained and washed several times with distilled water to give the desired product as a product in 97 % yield. The structure of Alkyl 2-chloroacetate was elucidated through the following reported procedure **[23].**

2.3.2. Synthesis of 3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,Ndimethylpropan-1-amine) [compound II]

Acetyl acetone (10 mmol) was subjected to condensation reaction with 20 mmol of 3-(N, N-dimethylamino)-1-propyl amine in the presence of 100 mL ethanol as appropriate solvent. The reaction contents were refluxed for 4-5 h at 70 $^{\circ}$ C and left to

cool and a product in a viscous liquid form will be produced. Purification of product will be done through extraction process by ethyl acetate to obtain the Schiff base compounds (**compound II**).

2.3.3. Synthesis of 3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N-(2-(alkyloxy)-2-oxoethyl)-N,N-dimethylpropan-1-aminium) chloride [SBGS-10, SBGS-14 and SBGS-16 compounds]

In a single-neck flask containing magnetic bar, a prepared compound **II** (10 mmole) was added to containing compound **I** (20 mmole) in diethyl ether as a solvent for 92 h at 25 $^{\circ}$ C with continuous stirring. Solid and viscous products were obtained. The unreacted materials were removed by washing the obtained products several times with diethylether to afford the required Schiff base cationic gemini surfactants (SBGS). The synthetic routes are represented in Fig. 1.

2.4. Electrodes and aggressive solutions for corrosion inhibition studies

The corrosion tests were carried out on the mild steel specimens with the chemical compositions (w %) Si 0.18%, C 0.16 %, Mn 0.71%, Ni 0.01 %, Cr 0.01%, S 0.04 % and Fe (balance). This electrode was used for one time. The cylindrical shaped of mild steel rod has a diameter of 0.5 cm, length of 3.0 cm and 4.55 cm² exposed area to fluid.

The aggressive solution of 1.0 M H_2SO_4 was prepared by diluting the analytical grade 98% H_2SO_4 with bi-distilled water. Various concentrations (0.01–1.0 mM) of the synthesized Schiff base gemini surfactants (SBGS) were also prepared in bi-distilled water and used as inhibitors for mild steel corrosion in 1.0 M H_2SO_4 .

2.5. Electrochemical Measurements

Electrochemical experiments were performed in a conventional three-electrode electrochemical cell with mild steel as working electrode, platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The reference electrode was coupled with a lugging capillary to ensure suitable geometry of cell electrodes for which potential drop is minimized. Before each electrochemical measurement, the mild steel was immersed in the test solution for 50-60 min to achieve a steady open circuit potential (OCP).

Electrochemical impedance spectroscopy measurements were performed with a phase-sensitive detector (amplifier) (Model 5208) driven by using VersaSTAT4 potentiostat/galvanostat with a frequency response analyzer (FRA) contained in a single unit under aerated conditions. Impedance spectra were recorded at E_{corr} in the frequency range 100 kHz to 0.5 Hz with the ac voltage amplitude of 10 mV.

Potentiodynamic polarization measurements were performed using VersaSTAT4 potentiostat/galvanostat under aerated conditions. Potentiodynamic anodic and cathodic polarization curves were obtained at a scan rate of 0.001 Vs⁻¹ in a potential range ± 250 mV versus the corrosion potential (E_{corr}). All electrochemical experiments were performed at 323 K.

2.6. Surface tension

The surface tension of SBGS compounds in water and 1.0 M H_2SO_4 was determined by Tensiometer- K6 processor (KRÜSS Company, Germany) via the ring method [24, 25], between the measurement runs, the ring was initially cleaned with pure water and acetone. All the measurements were performed at a constant temperature (298 K), which has been shown to be higher than the Krafft point of the investigated SBGS compounds (whereas the Krafft point of all three synthesized

surfactants were lower than 5 °C). All aqueous solutions of the synthesized compounds were remained to stand 2-3 h before determined. The values of surface tension were determined 3 times for each sample within 3 min interval between each reading and the values were taken as the average of these recorded values.

2.7. Electrical conductivity

Electrical conductivity measurements of Schiff base gemini surfactant solutions were done using a digital conductivity meter (model Type AD3000; EC/TDS and Temperature meter) at 298 K (above the Krafft point of prepared solutions). The measurement was repeated three times for each solution.

2.8. Biodegradability measurements

Biodegradability test of the synthesized Schiff base gemini surfactant in river water was measured by the surface tension method via Tensiometer-K6 processor (KRÜSS company, Germany) as reported in [23]. The calculation of biodegradation percent (D/%) was done as the following equation:

$$D\% = \frac{\gamma_t - \gamma_0}{\gamma_{bt} - \gamma_0} \times 100 \tag{1}$$

where the surface tension at time *t* is $\gamma_{\rm b}$ the surface tension at time zero is γ_0 , and the surface tension of river water without surfactant sample at time *t* is $\gamma_{\rm bt}$.

2.9. Surface morphological investigations

Freshly mild steel specimens were immersed in $1.0 \text{ M H}_2\text{SO}_4$ without and with 1.0 mM of SBGS-10, SBGS-14 and SBGS-16 inhibitors for 3 days at 323 K. The specimens were retrieved after 3 days, dried and used for the SEM analyses. SEM measurements were performed using scanning electron microscope (JEOL, model 5300) by applying operating voltage of 5 kV.

2.10. Computational simulation

The ground state geometries of the studied SBGS-10, SBGS-14 and SBGS-16 inhibitors were optimized with no constraints using the Density Functional Theory (DFT) based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) **[26-28]** and the 6-31G(d,p) basis set. Quantum chemical calculations were carried out using Gaussian-09 software package **[29]**. The conductor-like polarizable continuum model (CPCM) was applied to water as solution phase. The quantum chemical indices calculated were, total energy (E_{total}), the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap ($\Delta E = E_{LUMO}-E_{HOMO}$), the dipole moment (μ_{dipole}), the ionization potential (I_P), electron affinity (E_A), Chemical potential ($\mu_{potential}$), Global hardness (η), Global softness (σ), Electronegativity (χ), the fraction of electron transferred (ΔN) and Polarizability $<\alpha$ >. The molecular electrostatic potential (MEP) maps were generated in the range from deepest red color to deepest blue color to help in the explanation of the experimental data obtained for the corrosion process.

<<Figure 1>>

3. Results and discussion

3.1. Structure elucidation of the prepared Schiff base gemini surfactants (SBGS)

The spectroscopic results obtained from analysis of the prepared compounds are as follows:

3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethylpropan-1-amine) [compound II]: FT-IR (KBr pellet) shows characteristic bands at 2777-2946 cm⁻¹

(CH alipatic) and 1606 cm⁻¹ (CH=N), also showed the disappearance of two carbonyl band and $-NH_2$ band (**Figure S1, supporting data**).

3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N-(2-(decyloxy)-2-oxoethyl)-

N,N-dimethylpropan-1-aminium) chloride [SBGS-10]: Brownish-yellow semisolid, vield = 85%, FT-IR (KBr pellet) cm⁻¹ = 2920, and 2853 (v_{C-H} , aliphatic fatty chain), 1748 ($v_{C=0}$ of ester), 1211 (v_{C-O-C}) and 1611 (CH=N). ¹H NMR (400 MHz) δ (ppm) (DMSO- d_6): 0.77(t, 6H, 2[CH₃-CH₂]), 1.17(s, 28H, 2[(CH₃-CH₂)₇]), 1.42(t, 4H, 2[CH₂-N=C]) 1.62(s, 6H, 2[CH₃-C=N]), 1.75(m, 8H, 2[CH₂-CH₂O], $2[\underline{CH_2}-CH_2N]), 3.05(s, 12H, 4[\underline{CH_3}-N^+]), 3.12(s, 2H, [CH_2-C=N]), 3.81(m, 4H, 4H)$ $2[\underline{CH}_2-N^+]$, 4.41(s, 4H, 2[\underline{CH}_2-O]), 4.94(t, 4H, 2[\underline{CH}_2-CO]). ¹³C NMR (100 MHz) δ (ppm) (DMSO-*d*₆): 14.31[2(CH₃-CH₂)], 18.81[2(CH₃-C=N)], 22.41[2(CH₂-CH₂-CH₂-N⁺)], 25.44[2(CH₃-CH₂)], 28.28[2(-CH₂-CH₂-CH₂O)], 29.11[2(-CH₂-CH₂-CH₂O)], 29.48[2(CH₃CH₂-CH₂)₅], 39.58[CH₂-C=N]) 51.61[4CH₃-N⁺], 61.46[2CH₂-N=C], $66.28[2CO-CH_2-N^+)],$ $62.63[2CH_2-N^+],$ 95.57 [2**CH**₂-O], 164.21[2**C**=N], 165.34[2C=O, carbonyl ester].

3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-oxo-2-

(tetradecyloxy)ethyl)propan-1-aminium) chloride [SBGS-14]: Buff color, m.p = 88 °C, yield = 87%, FT-IR (KBr pellet) cm⁻¹ = 2955, and 2850(v_{C-H} , aliphatic <u>fatty</u> chain), 1749 ($v_{C=0}$ of ester), 1224 (v_{C-0-C}) and 1606 (CH=N) (Figure S2a; supporting data). ¹H NMR (400 MHz) δ (ppm) (DMSO-*d*₆): 0.61(t, 6H, 2[<u>CH₃-CH₂</u>]), 1.1(s, 44H, 2[(CH₃-<u>CH₂</u>)₁₁]), 1.37(t, 4H, 2[CH₂-N=C]) 1.62(s, 6H, 2[<u>CH₃-CH₂</u>)₁₁]), 1.37(t, 4H, 2[CH₂-N=C]) 1.62(s, 6H, 2[<u>CH₃-CH₂</u>]), 1.75(m, 8H, 2[<u>CH₂-CH₂O]</u>, 2[<u>CH₂-CH₂N]</u>), 3.04(s, 12H, 4[<u>CH₃-N⁺]</u>), 3.14(s, 2H, [CH₂-C=N]), 3.93(m, 4H, 2[<u>CH₂-CH₂N⁺]</u>), 4.37(s, 4H, 2[<u>CH₂-O]</u>), 4.71(t, 4H, 2[<u>CH₂-CH₂-N⁺]</u>), 4.37(s, 4H, 2[<u>CH₂-O]</u>), 4.71(t, 4H, 2[<u>CH₂-CH₂-CH₂-N⁺]</u>), 4.26[2(CH₃-CH₂)], 18.79[2(CH₃-C=N)], 22.47[2(CH₂-CH₂-N⁺)], 25.66[2(CH₃-CH₂-N⁺])]

CH₂)], 28.30[2(-CH₂-CH₂-CH₂O)], 29.09[2(-CH₂-CH₂-CH₂O)], 29.44[2(CH₃CH₂-CH₂O)], 39.56[CH₂-C=N]) 51.63[4CH₃-N⁺], 61.41[2CH₂-N=C], 62.61[2CH₂-N⁺], 66.26[2CO-CH₂-N⁺)], 95.54 [2CH₂-O], 163.14[2C=N], 165.29 [2C=O, carbonyl ester] (Figure S2c; supporting data).

3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-

(hexadecyloxy)-2-oxoethyl)propan-1-aminium) chloride [SBGS-16]: Pale brown color, m.p = 98 °C, yield = 90%, FT-IR (KBr pellet) cm⁻¹ = 2918, and 2851 (v_{C-H}, aliphatic <u>fatty</u> chain), 1749 (v_{C=O} of ester), 1196 (v_{C-O-C}) and 1608 (CH=N) (Figure 2a). ¹H NMR (400 MHz) δ (ppm) (DMSO-*d*₆): 0.86(t, 6H, 2[CH₃-CH₂]), 1.25(s, 52H, 2[(CH₃-CH₂)₁₃]), 1.62(t, 4H, 2[CH₂-N=C]) 1.91(s, 6H, 2[CH₃-C=N]), 1.95(m, 8H, 2[CH₂-CH₂O], 2[CH₂-CH₂N]), 2.51(s, 2H, [CH₂-C=N]), 3.23(s, 12H, 4[CH₃-N⁺]), 4.18(m, 4H, 2[CH₂-N⁺]), 4.59(s, 4H, 2[CH₂-O]), 4.96(t, 4H, 2[CH₂-CO]) (Figure 2b). ¹³C NMR (100 MHz) δ (ppm) (DMSO-*d*₆): 14.26[2(CH₃-CH₂)], 18.79[2(CH₃-C=N)], 22.47[2(CH₂-CH₂-N⁺)], 25.67[2(CH₃-CH₂)], 28.31[2(-CH₂-CH₂-CH₂O)], 29.09[2(-CH₂-CH₂-CH₂O)], 29.45[2(CH₃-CH₂)], 39.57[CH₂-C=N]) 51.63[4CH₃-N⁺], 61.44[2CH₂-N=C], 62.64[2CH₂-N⁺], 66.28[2CO-CH₂-N⁺)], 95.55 [2CH₂-O], 163.14[2C=N], 165.29 [2C=O, carbonyl ester] (Figure 2c).

<<Figure 2>>

3.2. Critical micelle concentration and surface-active properties

Studying the critical micelle concentration (CMC) of synthesized Schiff base gemini surfactants is a conventional method for the measurement of surface tension. The variations of the surface tension γ as a function of the surfactant molar concentration in water and 1.0 M H₂SO₄ at 298 K is shown in Fig. **3 a, b.** It is noted that the initial raise in the concentration of surfactant leads to the surface tension of the surfactant solutions decreased rapidly. At the break point, the surface tension

began to decrease slowly, indicating the formation of surfactant aggregations. The concentration value at the break point is shown as the CMC of the synthesized surfactants. Also it is found that the synthesized Schiff base gemini surfactants with longer hydrophobic chain have low CMC. Moreover, the values of CMC were decreased in 1.0 M H_2SO_4 compared with the values in water solutions (Table 1). These data indicated that the prepared Schiff base gimini surfactants are strongly adsorbed at steel/ H_2SO_4 interface.

Figure **4** represents the relation between electrical conductivity of synthesized Schiff base gemini surfactants solution (*k*) and concentration. In each of the plots, intersect at the point CMC have been obtained from two straight lines with different slopes. The CMC values calculated from electrical conductivity plots are recorded in Table **1**.

The degree of counter ion dissociation (α) can be obtained from the ratio of the slopes above and below the break indicative of the CMC, as shown in Fig 4. Normally, the degree of counter ion dissociation and the degree of counter ion binding (β) have the next relationship: β =1- α . The β parameter is an important for expression of how many counter ions are contained in the Stern layer to counterbalance the electrostatic force that opposes to the micelle formation [30]. All values of α and β are observed in Table 1, it also found that β values decreases slightly with longer hydrophobic alkyl chain at the certain temperature [31]. As well as from Table 1, it is noted that using electrical conductivity, the CMC values determined were in agreement with those obtained using surface tension.

From the critical micelle concentration data and surface tension values, the effectiveness values (the difference between the surface tension values of pure water

(γ_0) and the surface tension values at CMC (γ_{CMC}), π_{CMC}) were calculated according to the following expression (Eq. 2) [31]:

$$\pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC} \tag{2}$$

The maximum reduction of surface tension can be evaluated the effectiveness of synthesized surfactant to reduce the surface tension of water. The data in Table **1** showed that the increasing the hydrocarbon chain length led to increase π_{CMC} values. In addition to, the results showed that the synthesized SBGS-16 more effective surfactant and the maximum reduction of the surface tension at CMC reach to 36.27 mN m⁻¹ [**32**].

As well as at the air-water interface, the surface area A_{\min} showed the packing densities of Schiff base gemini surfactants, which is crucial to interpreting the surface activities of gemini surfactants. The value of Γ_{\max} describes the accumulation of surfactant molecules at the air-water interface and can be calculated via the Gibbs adsorption equation (3) [32]:

$$\Gamma_{\max} = \frac{-1}{2.303 nRT} \left(\frac{\mathrm{d}\gamma}{\mathrm{d}\log C} \right)_T$$
(3)

where *R* is a gas constant; *T* is the absolute temperature; C is the concentration of surfactant; γ is the surface tension at given concentration; $d\gamma/dlogC$ is the slope of γ vs log C; and *n* is the number of ionic species whose concentration at the interface varies with the surfactant concentration in the solution. The value of *n* is taken to be 3 for divalent gemini surfactants (the gemini amphiphile species and the two counter ions) [33, 34]. The minimum area occupied per surfactant molecule at the air/water interface (A_{\min} in nm²) is calculated by the following equation (4) [34]:

$$A_{\min} = \frac{10^{14}}{\Gamma_{\max} \times N_{A}}$$
(4)

where N_A is Avogadro's number. The values of Γ_{max} and A_{min} are listed in Table 1. From Table 1, it is found that the surfactant with a longer hydrophobic chain had a

higher A_{\min} value, suggesting that the decreasing in packing densities of gemini surfactants at the air-water interface with longer the hydrophobic tails. This rule is agreed with other gemini surfactants, and a possible explanation is that the increasing in hydrophobic chains length leads to a more prone to curl and thus make the A_{\min} value larger [35].

From Gibbs equations (Eqs. 5 and 6), the standard free energy change of micelle formation ($\Delta G_{\text{mic}}^{\circ}$) and adsorption ($\Delta G_{\text{ads}}^{\circ}$) of synthesized Schiff base surfactants were calculated according the following equations [36]:

$$\Delta G_{\rm mic}^0 = (2 - \alpha) RT \ln {\rm CMC}$$
(5)

$$\Delta G_{\rm ads}^0 = (2 - \alpha) RT \ln \text{CMC-} 0.06\pi_{\rm CMC} A_{\rm min}$$
(6)

where CMC is the critical micelle concentration, R is a gas constant, T = t+273, π_{CMC} is the effectiveness; α is a degree of counter ion dissociation and A_{\min} is the minimum area occupied per surfactant molecule at the air/water interface. The free energies values of micellization (ΔG_{\min}°) and adsorption (ΔG_{ads}°) of the synthesized Schiff base gemini surfactants (SBGS-10, SBGS-14 and SBGS-16) were calculated and are listed in Table 1. When the values of ΔG_{\min}° compared with the values of ΔG_{ads}° , it is noted that slightly increasing in ΔG_{ads}° values than ΔG_{\min}° values and the more negativity of values indicates the ability of these surfactants to adsorbed than micellization tendency due to the preference of adsorption is governed by the thermodynamic stability of the molecules at the air-water interface [37].

<<Figure 3>>

<<Figure 4>>

3.3. Biodegradability measurements of synthesized SBGS compounds

Using the surface tension method, the biodegradability in the river water of the synthesized cationic gemini surfactants was evaluated for 25 day. From Fig. 5, it is clear that gradually increasing in the biodegradability by increasing the time and reached to the maximum values after 25 day returned to the synthesized Schiff base gemini surfactants under investigation have ability to loss the surface activity. In addition to, there is a direct relationship between the hydrophobic chain length and the rate of biodegradation. So it is noted from Fig. 5 that the biodegradability increased by increasing the length of hydrophobic chain. Also due to the presence of an oxycarbonyl group (-O-C=O-) leads to increase the ability of investigated SBGS compounds to degrade by the action of the environmental microorganisms. Furthermore, the highest biodegradation extent was obtained in the case of SBGS-16 at 93%, SBGS-14 at 88% compared to SBGS-10 surfactants at 80%. The values of biodegradation of these synthesized Schiff base gemini surfactants specified them as biodegradable compounds. So the synthesized Schiff base gemini surfactants will be high biodegradability than the other synthesized surfactants and less toxicity, i.e., environment friendly [38]. In fact, the biodegradation affinity is which has the ability to degrade by the action of the environmental microorganisms.

<<Figure 5>>

3.4. Open circuit potential (Ecorr) vs. time measurement

 $E_{\rm corr}$ -time curves for mild steel in 1.0 M H₂SO₄ solution at 50 °C containing 1.0 mM of synthesized SBGS inhibitors is presented in Fig. 6. It is obvious from the curve that, $E_{\rm corr}$ of mild steel in the studied solution without surfactant is shifted to more noble direction until steady state potential is determined and the $E_{\rm corr}$ stabilized at around -471 mV (SCE). Upon the addition of surfactant molecules to the

aggressive system, a positive shift in E_{corr} is produced, i.e.; the potential was shifted to more noble direction [39]. In the presence of 1.0 mM of SBGS-10, SBGS-14 and SBGS-16, E_{corr} stabilized at -452, -459 and -466 mV (SCE), respectively. The divergence in E_{corr} in the aggressive medium with and without investigated inhibitors indicates that the metal surface was protected and covered by the surfactant adsorption.

<<Figure 6>>

3.5. Electrochemical impedance measurements (EIS)

The Nyquist, Bode phase and Bode modulus plots of mild steel in 1.0 M H₂SO₄ in the absence and presence of various concentrations of the investigated SBGS inhibitors is presented in Fig. 7 a-f. Nyquist diagram shown in Fig. 7 a, c and e exhibited that, the impedance plots consists of an inductive loop at low frequencies (LF) and a large capacitive loop at high frequencies (HF) both in the absence and presence of studied inhibitors. The inductive loop at LF generated from the adsorption relaxation of intermediates such as H^+_{ads} and SO_4^{2-} , displaying negative change in the surface coverage with potential on the metal surface [40]. The large capacitive loop at HF could be imputed to the double layer capacity in parallel with the charge transfer resistance (R_{ct}) . The occurrence of two time constants for steel corrosion at the corrosion potential value (E_{corr}) in the absence and presence of inhibitors has been reported [41]. Inspection of Fig. 7 a, c and e reveals that increase in the diameter of the Nyquist semicircles in the presence of the surfactants as compared to that without the inhibitors. This also increases with increase in the inhibitors dose. This suggests that the studied SBGS surfactants change the impedance response of mild steel in 1.0 M H₂SO₄ possibly due to adsorption of the surfactant molecules on the steel surface

and the degree of surface coverage by the adsorbed molecules increases with increase in inhibitor concentration in solution.

The depressed semicircular feature of the Nyquist plots is the characteristic of solid electrodes, and it is often regarded as frequency dispersion due to different possible forms of inhomogeneity **[42, 43]**. One other overt behavior of the Bode and phase modules in Fig. **7 b, d, f** especially in the presence of the surfactants is the appearance of the second time-constant at higher frequency, which suggests the formation and/or adsorption of intermediate corrosion products and/or steel-surfactant complexes. Moreover, phase plots reflect apparently higher values of the phase angles in the presence of the surfactants. These features can be attributed to the formation of protective films of the inhibitor molecules on the steel surface making it to exhibit relatively closer resemblance to an ideal capacitor than the metal surface in the acid blank system without the inhibitor molecules **[44]**.

The impedance data were analyzed by fitting to the equivalent circuit model as depicted in Fig. 8 for mild steel corrosion in 1.0 M H₂SO₄ and containing 1.0 mM SBGS-14. The circuit (Fig. 8 inset) consists of solution resistance R_s , the constant phase element (CPE) in parallel to the parallel charge transfer resistor, the charge transfer resistance, R_{ct} , in addition the inductive elements, R_L and L for H₂SO₄ corrosive medium. A CPE was used allowance of double-layer capacitance (C_{dl}) in the equivalent circuits in order to fit the data more accurately [45]. CPE have been used intensively to account for deviations brought about by surface roughness. The impedance of CPE can be represented as [46]:

$$Z_{\rm CPE} = \frac{1}{Y_0} \times \frac{1}{(j\omega)^n} \tag{7}$$

where j=(-1) is an imaginary number; ω is the angular frequency in rad s⁻¹ Q; Y_0 is the CPE constant and *n* is the CPE exponent which can be used as a criterion of the heterogeneity or roughness of the surface. For n = 1, a capacitance with $C = Y_0$, for n = -1, an inductance with $L = Y_0^{-1}$ and for n = 0.5, a Warburg element with $W = Y_0$. In this study, we can obtain Y_0 and *n* values, and transform Y_0 into C_{dl} using the following equation (8) [44]:

$$C_{\rm dl} = Y_0 (2\pi f_{\rm max})^{n-1}$$
 (8)

Here f_{max} is the frequency at a maximum point of imaginary part impedance. The impedance parameters including the R_{ct} , R_{s} , C_{dl} , Y_0 , R_{L} , n, L, R_{P} and the percentage inhibition efficiency values (P_{EIS} %) are reported in Table 2. The P_{EIS} and R_{p} were calculated from the R_{ct} values as [47]:

$$P_{\text{EIS}} / \% = \left(\frac{R_{\text{ct}}^{\text{i}} - R_{\text{ct}}^{\text{w}}}{R_{\text{ct}}^{\text{i}}}\right) \times 100$$

$$R_{\text{p}} = \frac{R_{\text{L}} \times R_{\text{ct}}}{R_{\text{L}} + R_{\text{ct}}}$$
(10)

where R_{ct}^{i} and R_{ct}^{w} are the charge transfer resistances with and without inhibitors, respectively. Results presented in the Table 2 reveal that the addition of studied Schiff base gemini surfactants to the aggressive solution increased the magnitude of R_{ct} , with corresponding decrease in C_{dl} , which implies that the SBGS inhibitors minimize the rate of charge transfer process associated with the corrosion reaction, and it is indicative of the corrosion inhibition characteristics of the studied SBGS surfactants [48, 49]. More so, the decrease in the C_{dl} in the presence of surfactants, which can result from a decrease in local dielectric constant or an increment in the thickness of the electrical double layer (or both), suggesting the formation of the protective layer of the inhibitor molecules on the steel surface act by adsorption at the steel/H₂SO₄

interface [50]. The decrease in C_{dl} is in accordance with Helmholtz model given by the following equation [49]:

$$C_{\rm d1} = \frac{\mathcal{E}_0 A}{d} \tag{11}$$

where ε is the dielectric constant of the medium, *d* is the thickness of the protective layer, *A* is the effective area of the electrode and ε_0 is the vacuum permittivity. Based on Helmholtz model (Eq. **11**), the decrease in the *C*_{dl} value demonstrates that the protective layer becomes thicker with increasing of inhibitor dose; this makes the corrosion inhibition more effective. Inspection of the data in Table **2**, it was found that, the values of inhibition efficiency for mild steel corrosion in 1.0 M H₂SO₄ increases with increase in concentration of SBGS inhibitors till reaching their maximum value at 1.0 mM. It is also visible from the data that *P*_{EIS}/% (SBGS-16) > *P*_{EIS}/% (SBGS-14)> *P*_{EIS}/% (SBGS-10) at all concentrations, which implies a better interaction of SBGS-16 on steel surface than the other compounds.

> <<Figure 7>> <<Figure 8>> <<Table 2>>

3.6. Potentiodynamic polarization (PDP) measurements.

The potentiodynamic polarization (PDP) curves for mild steel in 1.0 M solution of H_2SO_4 without and with various concentrations of the Schiff base gemini surfactants, and at 50 °C are shown in Fig. **9 a, b** and **c** for SBGS-10, SBGS-14 and SBGS-16, respectively. The polarization plot for mild steel in 1.0 M H_2SO_4 in the absence of the inhibitors shows initial sharp increase in both cathodic and anodic current densities attributed to the cathodic hydrogen reduction reaction and anodic partial reaction involving the early dissolution of mild steel [**51**]. The polarization

curves in the presence of the inhibitors show that SBGS-10, SBGS-14 and SBGS-16 compounds reduce both the cathodic and anodic corrosion current densities compared with those in H_2SO_4 free inhibitors. This indicates that the inhibitors act as adsorptive rust preventing materials, without proton reduction or metal dissolution at the metal/acid interface. That is, the investigated surfactants cover the active sites on the steel surface, which leads to the protection of metal surface against acid corrosive attacks and reduces oxidative dissolution and retards a hydrogen evolution reaction [52, 53].

Electrochemical kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (J_{corr}) and cathodic and anodic Tafel slopes (β_c and β_a , respectively) for the mild steel in all solutions (with and without inhibitors) were obtained using the Tafel extrapolation method. These values in addition to the value of the percentages of the inhibition efficiency (P_{PDP} , %) are listed in Table **3**. The values of corrosion current density in the absence (J_{corr}^0) and presence (J_{corr}^i) of the inhibitors were used to determine P_{PDP} and the surface coverage (θ) according to the equation (**12**) [**1**]:

$$P_{\rm PDP} / \% = \left(\frac{J_{\rm corr}^{\rm o} - J_{\rm corr}^{\rm i}}{J_{\rm corr}^{\rm o}}\right) \times 100 = \theta \times 100$$
(12)

Results in the Table **3** demonstrate that J_{corr} decreases significantly in the presence of SBGS compounds compared to the blank solution and also decreases with increasing concentration of the surfactant. In other words, the P_{PDP} increases with increase in concentration of the studied SBGS inhibitors. This indicates that as the concentration of the investigated surfactants increases, more molecules of the inhibitors or steel/surfactant complexes adsorb on the surface of mild steel thereby increasing the θ and also the P_{PDP} . This observation is a direct indication of the corrosion inhibition

characteristics of the studied SBGS compounds. The magnitude of the relative shift in $E_{\rm corr}$ after the addition of an inhibitor compared to the blank solution is often used to characterize an inhibitor an anodic, cathodic or mixed-type. A shift in $E_{corr} > \pm 85 \text{ mV}$ is generally attributed to an inhibitor of anodic or cathodic mitigating effect, while a shift in $E_{\text{corr}} < \pm 85 \text{ mV}$ implies that the inhibitor is of mixed effect, that is, it inhibits both anodic metal dissolution and cathodic reduction reaction [54, 55]. The data in Table 3 showed that for the studied Schiff base gemini surfactants, the shifts in $E_{\rm corr}$ over the whole concentration range are less than 85 mV, which implies that SBGS-10, SBGS-14 and SBGS-16 compounds are mixed-type inhibitors. The values of the cathodic (β_c) and anodic (β_a) Tafel slopes change with change in concentration. This suggests that the inhibitive actions of the studied surfactants are concentration dependent. The change in β_a values with change in concentration are generally more pronounced than change in β_c values. Moreover, β_c are also found to be greater than the respective β_a . This suggests that the inhibitors reduce the rate of the cathodic partial reaction by blocking the active sites involved in the cathodic hydrogen evolution without altering the mechanism of the cathodic reaction, while on the other hand, the anodic mild steel dissolution might have witnessed some change in mechanism as informed by the large change in β_a values, which is also inferable from the appearance of the anodic limiting current plateau in the polarization curves. A comparison of PPDP % values of SBGS-10, SBGS-14 and SBGS-16 as shown in Table **3** revealed that SBGS-16 exhibits better corrosion inhibition potentials than SBGS-10 and SBGS-14 over the concentration ranges considered in this study. Since the three studied surfactants differ in the length of the alkyl group "R" (R = 16 in SBGS-16; R = 14 in SBGS-14; R = 10 in SBGS-10) as shown in Fig. 9, it can be inferred that the higher P_{PDP} /% of SBGS-16 compared to SBGS-10 and SBGS-14 is as a result of the

increased alkyl chain length. Longer alkyl chain has been reported to favor higher P_{PDP} % due to increased adsorption at surface layers [56]. The efficiency order of the tested inhibitors at all concentrations is as follows: SBGS-16 > SBGS-14 > SBGS-10. This order is the same as the one obtained from EIS measurements.

<<Figure 9>>

<<Table 3>>

3.7. Adsorption Isotherm and thermodynamic parameters

In order to investigate the adsorption mechanism of corrosion inhibitor on steel/acid interface, adsorption isotherms were plotted. In the present study, the experimental data for the adsorption of SBGS-10, SBGS-14 and SBGS-16 inhibitors were subjected to various adsorption isotherms including the Flory-Huggins, Langmuir, Frumkin, Temkin and Freundlich isotherms. Among the different isotherm models tried, the most suitable one was selected with the help of regression coefficient R^2 (Table 4). Langmuir isotherm was found to be the most suitable mode to fit experimental data, with all linear R^2 very close to unity, indicating that adsorption process of I BGS-10, SBGS-14 and SBGS-16 on mild steel in 1.0 M H₂SO₄ obeys Langmuir isotherm. The linear form of the Langmuir isotherm is expressed as [2]:

$$\frac{\mathbf{C}_{i}}{\theta} = \mathbf{C}_{i} + \frac{1}{K_{ads}}$$
(13)

where C_i is the concentration of the inhibitors, θ , the degree of the coverage, K_{ads} is the equilibrium constant of adsorption process of corrosion inhibitors. The values of θ can be determined from the potentiodynamic polarization measurements by equation **12**. Plots of C_i/θ vs. C_i at 323 K give straight line as presented in Fig. **10**. The change

in Gibb's free energy of adsorption (ΔG_{ads}^{o}) is related to the K_{ads} by the equation (14)

[3]:

$$\Delta G_{\rm ads}^0 = -RT \ln(C_{\rm W} K_{\rm ads}) \tag{14}$$

where C_W is the molar concentration of water in acid solution which is 55.5 M [57], R is the gas constant and T is the absolute temperature. The values of ΔG_{ads}^{o} and K_{ads} for the studied SBGS inhibitors were calculated. Large values of K_{ads} imply better adsorption due to strong electrostatic interactions or enhanced charge transfer between the inhibitor molecules and steel surface. It can be seen that the values of K_{ads} follow the order: K_{ads} (SBGS-16; 15.38×10⁴) > K_{ads} (SBGS-14, 10.52×10⁴) > K_{ads} (SBGS-10; 6.82×10^4), which reveal that SBGS-16 possess stronger adsorption affinity onto the steel surface than SBGS-14 and SBGS-10, and thus SBGS-16 exhibits better inhibitive performance. Generally, adsorption of inhibitors on the surface of metal is classified as a physical adsorption mechanism, involving electrostatic interactions between the charged inhibitor molecules and the charged metal surface, when the value of ΔG_{ads}^{o} is less negative or around -20 kJ/mol. A value of ΔG_{ads}^{o} more negative or around -40 kJ/mol suggests that the adsorption of an inhibitor on the metal surface features chemisorption mechanism, involving charge sharing or charge transfer from organic inhibitor molecule to the metal surface to form a coordinate type of bond [57]. In the present study, the values of ΔG_{ads}^{o} obtained for SBGS-10, SBGS-14 and SBGS-16 were found to be -40.67, -41.84 and -42.85 kJ mol⁻¹, respectively, suggests that the surfactant molecules can adsorb on the metal surface with a typical of chemisorption mechanism, implying the formation of a stable protection layer [58]. This type of adsorption mechanism can be discussed in terms of the interaction between π electrons of surfactant molecules and vacant d-orbitals of metal surface to form coordination bonds by charge or electrons transfer [59].

<<Figure 10>>

<<Table 4>>

3.8. Surface characterization by SEM

The SEM images of mild steel specimens after the immersion in 1.0 M H₂SO₄ for 3 days in the absence and presence of 1.0 mM of SBGS-10, SBGS-14 and SBGS-16 compounds are shown in Fig. **11.** It can be seen from Fig. **11a** that the steel specimen in 1.0 M H₂SO₄ solution without inhibitors was strongly corroded and damaged due to free acid corrosion of the steel surface in the uninhibited corrosive environment, resulting in a heterogeneous and rough surface of mild steel in the investigated aggressive solution. In contrast, in presence of 1.0 mM of the investigated inhibitors, the surface morphology of the specimens was uncommonly improved resulting in the observation of smoother and less corroded surfaces (Fig. **11 b, c and d**). These micrographs confirmed the formation of protective layer on the surface of mild steel by the surfactant molecule, which shielding it from the direct acid attack and thereby minimizing the corrosion rate effectively. Moreover, the mild steel surface with SBGS-16 inhibitor (**Fig. 11d**) is smoother slightly than counterpart with SBGS-10 and SBGS-14 compounds, which also support the results obtained from EIS and PDP measurements.

<<Figure 11>>

3.9. Corrosion inhibition mechanism by SBGS compounds

The adsorption mechanism of the surfactant molecules at steel/acid interfaces is affected by the chemical structures of the surfactants, the nature and charged metal surface and the allocation of charge over the whole surfactant molecule. The hydrophobic chain length plays an important role in the corrosion inhibition of the

surfactant molecules. The results in Tables **2**, **3** reveal that the inhibition efficiency of the prepared SBGS compounds increments with increasing the hydrophobic chain length at the studied temperature. These chains are situated vertical to the steel surface **[14]**, that repulse the polar molecules from the surface of metal and consequently decreases the aggressive effects of the acid solution on the metal surface by formation of adsorbed monolayer on the metal surface **[60-62]**. The studied surfactants can adsorb on the steel surface through one and/or more of the following:

- **I.** Donor–acceptor interaction between the π -electron of double bond of carbonyl group and lone pair of electrons of nitrogen atoms of azomethine group (–CH=N–) and vacant d-orbital of the steel surface, which decreased the anodic dissolution of mild steel.
- II. Electrostatic interaction between the positive charge (quaternary nitrogen atom; N^+) on the prepared SBGS inhibitor and the already-adsorbed SO₄²⁻ ions, which decreased the evolution of hydrogen.
- III. Interaction between unshared electron pairs located at nitrogen and oxygen atoms and the vacant d-orbital of the steel surface.

The stability of the adsorbed monolayer on the steel surface may be due to the attraction forces occurring between the negatively charged metal surface and the positively charged head groups [63]. In addition to, the hydrophobic tail of the synthesized surfactants forms consecutive protective layers, which isolate the surface of steel from the aggressive acid solution.

3.10. Quantum chemical calculations

In this work theoretical measurements was used to investigate the inhibitory action of SBGS-10, SBGS-14 and SBGS-16 compounds in the gas and water media using B3LYP methods with 6-31G (d,p) basis set. Theoretical calculations can spread

light on experimental investigations or even predict some experimentally unknown properties [64]. The gas phase optimized structures and the respective HOMO and LUMO electron density surfaces of SBGS-10, SBGS-14 and SBGS-16 inhibitors are shown in Fig. 12.

3.10.1. Frontier molecular orbital (HOMO and LUMO orbitals) characteristic of

the investigated inhibitors

According to the theory of quantum chemistry [65, 66], the interaction between reactants only happens in frontier molecular orbital. To analyze the adsorption process of the corrosion inhibitors we take HOMO and LUMO of the compound molecules into consideration.

The E_{HOMO} indicates the ability of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals, whereas the E_{LUMO} indicates its ability to accept electrons. The lower the value of E_{LUMO} , the more ability of the molecule is to accept electrons [67].

The higher the value of E_{HOMO} of the inhibitor, the easier is its ability to offer electrons to the unoccupied d-orbital of metal surface, and the greater is its inhibition efficiency. As is seen from Table **5** by increasing the alkyl chain, SBGS-14 and SBGS-16 have the highest value of E_{HOMO} which indicates that have high inhibition efficiency. The E_{LUMO} of SBGS-14 and SBGS-16 inhibitors are lower than SBGS-10 which implies that better inhibition efficiency, but in water medium there is no trend observed.

The frontier molecular orbitals (FMO) distributions are of major importance in characterizing the adsorption priority of the inhibitors. The HOMO and LUMO molecular orbitals of the studied inhibitors are given in Fig. **12**. The results display that the HOMO orbitals are mostly localized on nitrogen and hydrogen (methyl

ammonium), which will probably give to the inhibitors a strong adsorption onto the mild steel surface throughout this site. furthermore, the HOMO orbitals are partially localized on the oxygen (carbonyl) indicating that it should be a probable adsorption site onto the mild steel surface as well but with less importance when compared to nitrogen and hydrogen (methyl ammonium). However, the LUMO is almost completely localized on the two chlorides and the second nitrogen (methyl ammonium).

The energy gap, ΔE between the HOMO and LUMO orbitals pointed the chemical reactivity of the studied inhibitors. The obtained values of ΔE indicate that the substitution of the hydrogen atom in SBGS-10 by butyl group (SBGS-14) or by hexyl group (SBGS-16) decreases the value of the energy gap. The smaller the value of ΔE , the more is the probable inhibition efficiency the compound has [68-70]. It was shown from Table 5 that inhibitors SBGS-14 and SBGS-16 have the smallest HOMO–LUMO gap compared with SBGS-10. Accordingly, SBGS-14 and SBGS-16 molecules have more inclination to adsorb on the metal surface than the SBGS-10 molecule.

3.10.2 . The dipole moment (μ_{dipole})

The dipole moment, μ_{dipole} , is the measurement of net molecular polarity. Popova et al., **[71]** declared that the high value of dipole moment encourage adsorption by affecting the transfer process through adsorbed layer. The energy of the deformability increases with the increase in μ_{dipole} , making the molecule easier to adsorb at the mild steel surface. The dipole moment of three inhibitors SBGS-10, SBGS-14 and SBGS-16 show the same trend as obtained for the energy gap.

3.10.3 .Total energy (E_{total})

The total energy values of the studied SBGS models are listed in Table 5. The

order of increasing total energy of the undertaken inhibitors is as follows:

$$E_{\text{total}}$$
 (SBGS-10) < E_{total} (SBGS-14) < E_{total} (SBGS-16)

This result indicated that SBGS-16 inhibitor is favorably adsorbed through the active centers of adsorption on onto the mild steel surface.

3.10.4 . Ionization potential (I_P) and electron affinity (E_A)

Ionization potential (I_P) and electron affinity (E_A) are related to the energy of the HOMO and the LUMO according to Koopman's theorem [72].

$$I_{\rm P}=-E_{\rm HOMO} \tag{15}$$

$$E_{\rm A} = -E_{\rm LUMO} \tag{16}$$

Ionization potential is defined as the amount of energy required to remove an electron from a molecule. High Ionization energy show chemical inertness and small ionization energy show high reactivity of the atoms and molecules **[73]**. In this study ionization potential of SBGS-14 and SBGS-16 have lower value than SBGS-10 indicates that SBGS-14 and SBGS-16 possesses high inhibition efficiency.

3.10.5. Electronegativity (χ), chemical hardness (η) and chemical softness (σ)

The electronegativity (χ) and chemical hardness (η) were estimated as linear combinations of the calculated I_p and E_A [72]:

$$\chi = \mu_{\text{potential}} = \frac{I_{\text{P}} + E_{\text{A}}}{2}$$

$$\eta = \frac{I_{\text{P}} - E_{\text{A}}}{2}$$
(17)
(18)

Chemical softness (σ) is the inverse of the hardness [74] estimated by using the equation (19):

$$\sigma = \frac{1}{\eta} \tag{19}$$

The order of electronegativity of the studied inhibitors are shown in Table **5** as SBGS- $10 > SBGS-14 \approx SBGS-16$. According to Sanderson's electronegativity equalization

principle [75], an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order SBGS-10 < SBGS-14 \approx SBGS-16. With a high electronegativity and low difference of electronegativity speedily reaches equalization and low reactivity is expected which in turn marks low inhibition efficiency.

The molecular reactivity of the corrosion inhibitors are investigated from chemical hardness (η) and softness (σ) [76]. It is obvious that the chemical hardness principally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions, or molecules under small perturbation of chemical reaction [77, 78]. These quantities are connected with the Lewis theory of acid and bases and Pearson's hard and soft acids and bases [79]; a hard molecule has a large energy gap ΔE and a soft molecule has a small energy gap ΔE . Soft molecules are more interactive than hard ones because they could easily offer electrons to an acceptor. Adsorption occurs most likely at the region of the molecule where σ has the highest value [80]. In a corrosion system, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid. Bulk metals are soft acids and thus soft base inhibitors are most effective for acidic corrosion of these metals. The order of the inhibitors according to softness value was found to be SBGS-16 \approx SBGS-14 > SBGS-10.

3.10.6. The global electrophilicity (ω)

The global electrophilicity index (ω) introduced by Parr **[80]** as a measurement of energy reducing due to maximal electron flow between donor and acceptor and is given by equation **(20) [80]**:

$$\omega = \frac{\mu_{\text{potential}}^2}{2\eta} \tag{20}$$

Electrophilicity provide information on the nucleophilic or electrophilic nature of the molecule. A good nucleophilic is recognized by lower value of chemical potential and electrophilicity and reciprocally a good electrophilic is recognized by a high value of

chemical potential and electrophilicity. In this study SBGS-14 and SBGS-16 are strongest nucleophile.

This index measures the propensity of chemical species to accept electrons [81]. A good, more reactive, nucleophile is characterized by lower value of ω ; and conversely a good electrophile is characterized by a high value of ω . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

3.10.7. Natural bond orbital analysis (NBO)

Since atomic charges affects the electrostatic interactions of the compounds. Thus, atomic charges are used for the characterization of the molecular polarity of molecules. The total atomic charges of the SBGS-10, SBGS-14 and SBGS-16 inhibitors are calculated using NBO [82] analysis as implemented in the Gaussian 09 program with B3LYP/6-31G (d,,p) method and the results are shown in Figure 13. It is well known that the hetero atom with more negative charge is more reactive toward the interaction with the metal surface [83, 84]. So, from the resulted values one can conclude that nitrogen atoms and oxygen atoms possess the highest negative atomic charges indicating that the compounds can effectively inhibit the corrosion of the steel through adsorption on its surface via their active sites (N and O atoms).

3.10.8. The fraction of electron transferred (ΔN) and electrostatic potential maps

The fraction of electron transferred can be calculated according to Pearson theory [85].

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm inh}}{2(\eta_{\rm Fe} + \eta_{\rm inh})}$$
(21)

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule, respectively, η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe} =7.0 eV [86]

and $\eta_{\text{Fe}}=0$ is used assuming that for a metallic bulk $I_{\text{p}}=E_{\text{A}}$ [87] because they are softer than the neutral metallic atoms.

From Lukovits's study [81]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: SBGS-16 \approx SBGS-14 > SBGS-10. The results denote that ΔN values correlates highly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is connected with the best inhibitor, whereas the least fraction is connected with the inhibitor that has the least inhibition efficiency.

Gomez et al., **[88]** proposed simple charge transfer model for donation and back-donation of charges which gives the information that the electronic back-donation process can be occurring controlling the interaction between the inhibitor molecule and the metal surface. The concept confirms that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is related to the hardness of the molecule, as shown in equation (22) **[88].**

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \tag{22}$$

The $\Delta E_{\text{Back-donation}}$ means that when $\eta > 0$ then $\Delta E_{\text{Back-donation}} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored [85]. The values of $\Delta E_{\text{Back-donation}}$ follow the order SBGS-10 < SBGS-14 \approx SBGS-16 which indicates that back-donation is favored for the SBGS-14 and SBGS-16 inhibitors.

Molecular electrostatic potential MEPs are studied for all the optimized structures (Fig. 14). In all the structures the negative charge density is localized on the

nitrogen (methyl ammonium), and oxygen (carbonyl) atoms indicating a high ability in metal coordination

3.10.9. Polarizability (<α>)

The electric dipole polarizability, $(<\alpha>)$ is another global property that provides information about the distribution of electrons, which can be calculated using equation (23) [89--91]:

$$<\alpha>=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$$
(23)

According to Table **5** SBGS-16 inhibitor has the highest polarizability which probably increases its adsorption on the metal surface and increases the inhibition efficiency.

3.10.10. Quantitative Structure–Activity Relationships (QSAR)

Quantitative Structure–Activity Relationships (QSAR) is used to relate the quantum chemical parameters to experimental inhibition efficiency of the studied inhibitors and drive the mathematical relationships [59, 92, 93]. The non-linear mathematical model [94] is used to correlate quantum chemical parameters (E_{HOMO} , E_{LUMO} , energy gap, dipole moment, polarizability and the fraction of electron transfer) at different inhibitor concentrations C_i, with the experimental inhibition efficiencies. The non-linear model has the form [59]:

$$P_{\rm cal} / \% = \frac{(AX_{\rm j} + B)C_{\rm i}}{1 + (AXj + B)C_{\rm i}} \times 100$$
(24)

where *A* and *B* are constants obtained by regression analysis; X_j is a quantum chemical index characteristic for the molecule *j* and C_i denotes the inhibitor concentration. The obtained equations for the non linear model in the case of gas and water media respectively are as follow [59]:

$$P_{\text{cal}} / \% = \frac{(-30800E_{\text{HOMO}} - 43117E_{\text{LUMO}} + 107630\Delta E + 17977\mu + 63923\Delta N + 283\alpha + 162226) \times C_{\text{i}}}{1 + (-30800E_{\text{HOMO}} - 43117E_{\text{LUMO}} + 107630\Delta E + 17977\mu + 63923\Delta N + 283\alpha + 162226) \times C_{\text{i}}} \times 100$$
(25)

$$P_{cal} / \% = \frac{(-27957E_{HOMO} - 3.5E_{LUMO} + 70302\Delta E + 14138\mu - 160367\Delta N + 227\alpha + 162462) \times C_{i}}{1 + (-27957E_{HOMO} - 3.5E_{LUMO} + 70302\Delta E + 14138\mu - 160367\Delta N + 227\alpha + 162462) \times C_{i}} \times 100$$
 (26)

The calculated efficiencies from the equations 25 and 26, at different concentrations of the studied inhibitors are given in Table 3. In gas and water media the nonlinear method gives correlation coefficient r=0.85 and low determination coefficient $R^2=0.72$ that not accepted.

To improve the deviation, linear model is used to correlate quantum chemical parameters (polarizability α and total energy TE) at 1.0 mM inhibitor concentrations C_i, with the experimental inhibition efficiencies. In gas and water media the obtained equations for linear model are as follow:

$$P_{\rm cal} / \% = -1.7913TE - 6.1829\alpha - 2041.4451$$
⁽²⁷⁾

$$P_{\rm cal} / \% = -9.6009TE - 26.8799\alpha - 11113.6680$$
 (28)

The linear method gives good and accepted determination coefficient $R^2=1.00$ and residual sum of squares: rss = 3.7201×10^{-11} for gas medium. In water medium Coefficient of Determination $R^2 = 0.999$ and Residual Sum of Squares: rss= 9.3854×10^{-7} .

4. Conclusions

Three Novel Schiff Base-based cationic gemini surfactants, SBGS-10, SBGS-14 and SBGS-16 have been synthesized, characterized and applied as potentials inhibitors for mild steel corrosion in 1.0 M H₂SO₄. The following conclusions can be drawn from the results.

- 1. All synthesized surfactants inhibit mild steel corrosion in 1.0 M H_2SO_4 showing the *P* as high as 99.21 % at 1.0 mM and 323 K, and the *P* increases with increasing the inhibitor concentrations.
- **2.** Potentiodynamic polarization measurements revealed that the studied surfactants are mixed-type corrosion inhibitors.
- **3.** Increasing the hydrophobic chain length increased the efficiency due to greater adsorption on the metal surface.
- 4. The adsorption model obeys to the Langmuir isotherm, and the high negative values of the Gibbs free energy indicate chemical adsorption capability of SBGS compounds on steel surface.
- **5.** SEM analyses confirmed the formation of protective film of the surfactant molecules on the steel surface thereby preventing it from direct acid attack.
- 6. Quantum parameters such as E_{HOMO} , E_{LUMO} , band gap, (ΔE), dipole moment, hardness, softness, electrophilicity index, fraction of electrons transferred, NBO charges etc. were calculated using DFT at B3LYP/6-31G (d,p) level of theory and were correlated with the inhibition efficiencies of the studied inhibitors. According to the QSAR's linear model of three inhibitors give good determination coefficient R^2 =1.00 using polarizability and total energy chemical parameters at 1.0 mM inhibitor concentrations with the experimental inhibition efficiencies.
- 7. The results obtained from both experimental and theoretical studies indicated that the trend of P/% of the investigated Schiff base gemini surfactants is: SBGS-16> SBGS-14> SBGS-10.

Consequently, all results showed that, the synthesized compounds are biodegradable and good inhibitors for mild steel in H_2SO_4 solution.

<u>Appendix A. Supplementary material</u>

Figure S1: FT-IR *3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethylpropan-1-amine)* [compound II] and <u>Figure S2</u>: FT-IR (a) ¹H NMR (b) and ¹³C NMR (c) spectra of 3,3'-(pentane-2,4-diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-0x0-2-(tetradecyloxy)ethyl)propan-1-aminium) chloride [SBGS-14].

Acknowledgments

The authors would like to thank King Faisal University, College of Science, Chemistry department and Sohag University, Faculty of Science, chemistry department, and corrosion laboratory for facilitating the study.

References

- H. M. Abd El-Lateef, M. Ismael, I. M.A. Mohamed, Novel Schiff base amino acid as corrosion inhibitors for carbon steel in CO₂-saturated 3.5% NaCl solution: experimental and computational study, Corro. Rev., 33 (2015) 77–97.
- H. M. Abd El-Lateef, Experimental and Computational Investigation on the Corrosion Inhibition Characteristics of mild steel by some novel synthesized imines in Hydrochloric acid Solutions, Corros. Sci., 92 (2015) 104–117.
- 3. H. M. Abd El-Lateef, Synergistic effect of polyethylene glycols and rare earth Ce⁴⁺ on the corrosion inhibition of carbon steel in sulfuric acid solution: electrochemical, computational, and surface morphology studies, Res. Chem. Intermed., 42 (2016) 3219–3240.
- 4. H. M. Abd El-Lateef, V.M. Abbasov, L.I. Aliyeva, E.E. Qasimov, I. T. Ismayilov, Inhibition of carbon steel corrosion in CO₂-saturated brine using some newly surfactants based on palm oil: Experimental and theoretical investigations, Mater. Chem. Phys., 142 (2013) 502-512.

- A. Yousefi, S. Javadian, J. Neshati, A new Approach to Study the Synergistic Inhibition Effect of Cationic and Anionic Surfactants on the Corrosion of Mild Steel in HCl Solution, Ind. Eng. Chem. Res., 53 (2014) 5475–5489.
- **6.** M. A. Quraishi, D. Jamal, Inhibition of mild steel corrosion in the presence of fatty acid triazoles, J. Appl. Electrochem., 32 (2002) 425-430.
- **7.** F. Khaled, K. Babić-Samardžija, N. Hackerman, Piperidines as corrosion inhibitors for iron in hydrochloric acid, J. Appl. Electrochem., 34 (2004) 697-704.
- H.-L. Wang, R.-B. Liu, J. Xin, Inhibiting effects of some mercapto-triazole derivatives on the corrosion of mild steel in 1.0 M HCl medium. Corros. Sci. 46 (2004) 2455-2466.
- **9.** S. M. A. Shibli, V. S. Saji, Co-inhibition characteristics of sodium tungstate with potassium iodate on mild steel corrosion. Corros. Sci. 47 (2005) 2213–2224.
- M. Christov, A. Popova, Adsorption characteristics of corrosion inhibitors from corrosion rate measurements. Corros. Sci. 46 (2004) 1613–1620.
- M. S. Morad, A. M. Kamal El-Dean, 2, 2'-Dithiobis (3-cyano-4, 6dimethylpyridine): A new class of acid corrosion inhibitors for mild steel. Corros. Sci. 48 (2006) 3398–3412.
- 12. D. Asefi, M. Arami, N. M. Mahmoodi, Electrochemical effect of cationic gemini surfactant and halide salts on corrosion inhibition of low carbon steel in acid medium, Corros. Sci. 52 (2010) 794–800.
- X. Wang, H. Yang, F. Wang, Inhibition performance of a gemini surfactant and its co-adsorption effect with halides on mild steel in 0.25 M H₂SO₄ solution, Corros. Sci. 55 (2012) 145–152.
- 14. I. Aiad, D. Emam, A. El-Deeb, E. Abd-Alrahman, Novel Imidazolium-Based Gemini Surfactants: Synthesis, Surface Properties, Corrosion Inhibition and

Biocidal Activity Against Sulfate-Reducing Bacteria, J. Surfact. Deterg. 16 (2013) 927–935.

- 15. M.A. Hegazy, A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution, Corro. Sci., 51 (2009) 2610–2618.
- 16. S. Zhu, F. Cheng , J. Wang, J.-G. Yu, Anionic Gemini surfactants: Synthesis and aggregation properties in aqueous solutions, Colloids and Surfaces A: Physicochem. Eng. Aspects 281 (2006) 35–39.
- **17.** S. M. Tawfik, Synthesis, surface, biological activity and mixed micellar phase properties of some biodegradable gemini cationic surfactants containing oxycarbonyl groups in the lipophilic part, J. Ind. Eng. Chem., 28 (2015) 171–183.
- R. Kamboj, S. Singh, A. Bhadani, H. Kataria, G. Kaur, Gemini imidazoliumsurfactants: synthesis and their biophysiochemical study, Langmuir, 28 (2012) 11969–11978.
- Y. K. Agrawal, J. D. Talati, M. D. Shah, M. N. Desai and N. K. Shah, Schiff bases of ethylenediamine as corrosion inhibitors of zinc in sulphuric acid, Corros. Sci., 46 (2004) 633–651.
- 20. K. C. Emregul, R. Kurtaran and O. Atakol, An investigation of chloridesubstituted Schiff bases as corrosion inhibitors for steel, Corros. Sci., 45 (2003) 2803–2817.
- 21. H. M. Abd El-Lateef, A. M. Abu-Dief, L. H. Abdel-Rahman, E. C. Sañudo, N. Aliaga-Alcalde, Electrochemical and theoretical quantum approaches on the inhibition of C1018 carbon steel corrosion in acidic medium containing chloride using some newly synthesized phenolic Schiff bases compounds, J. Electroanal. Chem., 743 (2015) 120–133.

- 22. M. Mobin, S. Masroor, Adsorption and Corrosion Inhibition Behavior of Schiff Base-Based Cationic Gemini Surfactant on Mild Steel in Formic Acid, J. Disper. Sci. Technol., 35 (2014) 535–543.
- **23.** H. M. Abd El-Lateef, M. A. Abo-Riya, A. H. Tantawy, Empirical and quantum chemical studies on the corrosion inhibition performance of some novel synthesized cationic Gemini surfactants on carbon steel pipelines in acid pickling processes, Corro. Sci., 108 (2016) 94–110.
- 24. Y. Zhu, M. L. Free, Experimental investigation and modeling of the performance of pure and mixed surfactant inhibitors: Micellization and corrosion inhibition, Colloids and Surfaces A: Physicochem. Eng. Aspects, 489 (2016) 407–422.
- 25. Y. Zhu, M. L. Free, Experimental Investigation and Modeling of the Performance of Pure and Mixed Surfactant Inhibitors: Partitioning and Distribution in Water-Oil Environments, J. Electrochem. Soc., 162 (2015) C702-C717.
- A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, Chem. Phys., 98 (1993) 5648.
- 27. A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A., 38 (1988) 3098.
- **28.** C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B., 37 (1988) 785.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.

Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.
C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J.
E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.
Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.
Martin, K. Morokuma, V. G. Zakr- zewski, G. A. Voth, P. Salvador, J. J.
Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J.
Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

- 30. P. Quagliotto, G. Viscardi, C. Barolo, E. Barni, S. Bellinvia, E. Fisicaro, C. Compari. Gemini pyridinium surfactants: synthesis and conductometric study of a novel class of amphiphiles, J. Org. Chem., 68 (2003) 7651-7660.
- 31. X. Zhong, J. Guo, L. Feng, X. Xu, D. Zhu, Cationic Gemini Surfactants Based on Adamantane: Synthesis, Surface Activity and Aggregation Properties, Colloid Surface A., 441 (2014) 572–580.
- 32. R. Mousli and A. Tazerouti, Synthesis and Some Surface Properties of Glycine-Based Surfactants, J. Surfact. Deterg., 14 (2011) 65-72.
- **33.** R. Zana, Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review, Adv. Colloid Interface Sci. 97 (2002) 205–253.
- 34. M. Q. Ao, G. Y. Xu, Y. Y. Zhu, Y. Bai, Synthesis and properties of ionic liquidtype Gemini imidazolium surfactants, J. Colloid Interface Sci., 326 (2008) 490– 495.
- 35. L. M. Zhou, X. H. Jiang, Y. T. Li, Z. Chen, X. Q. Hu, Synthesis and properties of a novel class of gemini pyridinium surfactants, Langmuir, 23 (2007) 11404–11408.
- **36.** H. M. Abd El-Lateef, A. H. Tantawy, Synthesis and evaluation of novel series of Schiff base cationic surfactants as corrosion Inhibitors for Carbon Steel in

Acidic/Chloride Media: experimental and theoretical investigations, RSC Adv., 6 (2016) 8681-8700.

- 37. S. M. Tawfik, A. A. Abd-Elaal, S. M. Shaban, A. A. Roshdy, Surface, thermodynamic and biological activities of some synthesized Gemini quaternary ammonium salts based on polyethylene glycol, J. Ind. Eng. Chem., 30 (2015) 112–119.
- 38. L. Pérez, A. Pinazo, M T. Garcia, M. Lozano, A. Manresa, M. Angelet, M. P. Vinardell, M. Mitjans, R. Pons, M. R. Infante, Cationic surfactants from lysine: synthesis, micellization and biological evaluation, Eur. J. Med. Chem., 44 (2009) 1884-1892.
- **39.** Y. Zhu, M. L. Free, G. Yi, Electrochemical measurement, modeling, and prediction of corrosion inhibition efficiency of ternary mixtures of homologous surfactants in salt solution, Corro. Sci., 98 (2015) 417–429.
- **40.** P. C. Okafor, Y. Zheng, Synergistic inhibition behaviour of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H_2SO_4 solutions, Corros. Sci., 51 (2009) 850–859.
- **41.** S. A. Umoren, Y. Li, F. H. Wang, Synergistic effect of iodide ion and polyacrylic acid on corrosion inhibition of iron in H₂SO₄ investigated by electrochemical techniques, Corros. Sci. 52 (2010) 2422–2429.
- 42. B. Wang, M. Du, J. Zhang, C.J. Gao, Electrochemical and surface analysis studies on corrosion inhibition of Q235 steel by imidazoline derivative against CO₂ corrosion, Corros. Sci., 53 (2011) 353–361.
- **43.** L. R. Chauhan, G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium, Corros. Sci., 49 (2007) 1143-1161.

- 44. H. M. Abd El-Lateef, A. M. Abu-Dief, B. E. M. El-Gendy, Investigation of adsorption and inhibition effects of some novel anil compounds towards mild steel in H₂SO₄ solution: Electrochemical and theoretical quantum studies, J. Electroanal. Chem., 758 (2015) 135–147.
- **45.** M. Ascencio, M. Pekguleryuz, S. Omanovic, An investigation of the corrosion mechanisms of WE43 Mg alloy in a modified simulated body fluid solution: The influence of immersion time, Corros. Sci., 87 (2014) 489–503.
- **46.** A. Popova, M. Christov, Evaluation of impedance measurements on mild steel corrosion in acid media in the presence of heterocyclic compounds, Corros. Sci., 48 (2006) 3208-3221.
- 47. V. M. Abbasov, H. M. Abd El-Lateef, L. I. Aliyeva, E. E. Qasimov, I. T. Ismayilov, M. M. Khalaf, A study of the corrosion inhibition of mild steel C1018 in CO₂-saturated brine using some novel surfactants based on corn oil, Egypt J. Petrol. 22 (2013) 451–470.
- **48.** Z. Tao, S. Zhang, W. Li, B. Hou, Adsorption and inhibitory mechanism of 1H-1,2,4-triazol- 801 1-yl-methyl-2-(4-chlorophenoxy) acetate on corrosion of mild steel in acidic solution, Ind. Eng. Chem. Res., 50 (2011) 6082-6088.
- 49. N. S. Ayati, S. Khandandel, M. Momeni, M. H. Moayed, A. Davoodi, M. Rahimizadeh, Inhibitive effect of synthesized 2-(3-pyridyl)-3,4-dihydro-4-quinazolinone as a corrosion inhibitor for mild steel in hydrochloric acid, Mater. Chem. Phys., 126 (2011) 873-879.
- 50. O. A. Hazazi, A. Fawzy, M. Awad, Synergistic Effect of Halides on the Corrosion Inhibition of Mild Steel in H₂SO₄ by a Triazole Derivative: Kinetics and Thermodynamic Studies, Int. J. Electrochem. Sci., 9 (2014) 4086 – 4103.

- **51.** H. J. Flitt, D. P. Schweinsberg, Evaluation of corrosion rate from polarization curves not exhibiting a Tafel region, Corros. Sci., 47 (2005) 3034–3052.
- 52. G. Gece, Drugs: A review of promising novel corrosion inhibitors, Corros. Sci.,53 (2011) 3873–3898.
- **53.** A. El-Sayed, A. M. Shaker, H. M. Abd El-Lateef, Corrosion inhibition of tin, indium and tin-indium alloys by adenine or adenosine in hydrochloric acid solution, Corros. Sci., 52 (2010) 72-81.
- 54. J. N. Asegbeloyin, P. M. Ejikeme, L. O. Olasunkanmi, A. S. Adekunle, E. E. Ebenso, A novel Schiff base of 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one and 2,2'- (ethylenedioxy)diethylamine as potential corrosion inhibitor for mild steel in acidic medium, Mater., 8 (2015) 2918-2934.
- **55.** L. C. Murulana, M. M. Kabanda, E. E. Ebenso, Experimental and theoretical studies on the corrosion inhibition of mild steel by some sulphonamides in aqueous HCl. RSC Adv., 5 (2015) 28743-28761.
- 56. L. C. Murulana, A. K. Singh, S. K. Shukla, M. M. Kabanda, E. E. Ebenso, Experimental and quantum chemical studies of some bis (trifluoromethylsulfonyl) imide imidazolium-based ionic liquids as corrosion inhibitors for mild steel in hydrochloric acid solution, Ind. Eng. Chem. Res., 51 (2012) 13282-13299.
- 57. Y. Qiang, S. Zhang, S. Xu, W. Li, Experimental and theoretical studies on the corrosion inhibition of copper by two indazole derivatives in 3.0% NaCl solution, J. Colloid Interf. Sci., 472 (2016) 52–59.
- 58. J. Zhang, X.L. Gong, H.H. Yu, M. Du, The inhibition mechanism of imidazoline phosphate inhibitor for Q235 steel in hydrochloric acid medium, Corros. Sci., 53 (2011) 3324–3330.

- 59. Y. Zhu, M. L. Free, G. Yi, Experimental Investigation and Modeling of the Performance of Pure and Mixed Surfactant Inhibitors: Aggregation, Adsorption, and Corrosion Inhibition on Steel Pipe in Aqueous Phase, J. Electrochem. Soc. 162(10) (2015) C582-C591.
- 60. A. U. Ezeoke, O. G. Adeyemi, O. A. Akerele and N. O. Obi-Egbedi, Computational and Experimental Studies of 4-Aminoantipyrine as Corrosion Inhibitor for Mild Steel in Sulphuric Acid Solution, Int. J. Electrochem. Sci., 7 (2012) 534–553.
- **61.** A. Frignani, V. Grassi, F. Zanotto and F. Zucchi, Inhibition of AZ31 Mg alloy corrosion by anionic surfactants, Corros. Sci., 63 (2012) 29–39.
- A. Balbo, A. Frignani, V. Grassi and F. Zucchi, Corrosion inhibition by anionic surfactants of AA2198 Li-containing aluminium alloy in chloride solutions, Corros. Sci., 73 (2013) 80–88.
- **63.** N. A. Negm, I. Aiad, Synthesis and characterization of multifunctional surfactants in oil-field protection applications, J. Surf. Deterg., 8 (2007) 87–92.
- 64. L. Guo, S. Zhu, S. Zhang, Q. He, W. Li, Theoretical studies of three triazole derivatives as corrosion inhibitors for mild steel in acidic medium, Corros. Sci., 87 (2014) 366-375.
- 65. G. Bereket, E. Hür, C. Öğretir, Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium, J. Mol. Struct., 578 (2002) 79-88.
- **66.** F. Kandemirli, S. Sagdinc, Theoretical study of corrosion inhibition of amides and thiosemicarbazones, Corros. Sci., 49 (2007) 2118–2130.
- **67.** G. Gao, C. Liang, Electrochemical and DFT studies of β-amino-alcohols as corrosion inhibitors for brass, Electrochim. Acta., 52 (2007) 4554-4559.

- 68. Y. Qiang, L. Guo, S. Zhang, W. Li, Sh.Yu, J. Tan, Synergistic effect of tartaric acid with 2,6-diaminopyridine on the corrosion inhibition of mild steel in 0.5 M HCl. Sci. Rep. 6, 33305; doi: 10.1038/srep33305 (2016).
- **69.** G. Gece, S. Bilgic, Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media, Corros. Sci., 51 (2009) 1876-1878.
- 70. X. Li, S. Deng, X. Xie, Experimental and theoretical study on corrosion inhibition of oxime compounds for aluminium in HCl solution, Corros. Sci., 81 (2014) 162–175.
- **71.** A. Popova, M. Christov, T. Deligeorgiev, Influence of the molecular structure on the inhibitor properties of benzimidazole derivatives on mild steel corrosion in 1.0 M hydrochloric acid, Corros., 59 (2003) 756-764.
- 72. C. C. Zhan, J. A. Nichols, D. A. Dixon, Ionization potential, electron affinity, electronegativity, hardness, and electron excitation energy: molecular properties from density functional theory orbital energies, J. Phys. Chem. A, 107 (2003) 4184-4195.
- **73.** Y. Zhua, M. L. Freea, J.-H. Choa, Integrated evaluation of mixed surfactant distribution in water-oil-steel pipe environments and associated corrosion inhibition efficiency, Corros. Sci., 110 (2016) 213–227.
- 74. I. B. Obot, D. D. Macdonald, Z. M. Gasema, Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview, Corros. Sci., 99 (2015) 1–30.
- 75. P. Geerlings, F. D. Proft, Chemical Reactivity as Described by Quantum Chemical Methods, Int. J. Mol. Sci., 3 (2002) 276-309.

- 76. N.O. Obi-Egbedi, I.B. Obot, Inhibitive properties, thermodynamic and quantum chemical studies of alloxazine on mild steel corrosion in H₂SO₄, Corros. Sci., 53 (2011) 263–275.
- 77. H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat,, R. Touzani, M. Elazzouzi, Theoretical approach to the corrosion inhibition efficiency of some pyrimidine derivatives using DFT method of mild steel in HCl solution, J. Chem. Pharm. Res., 6 (2014) 1216-1224.
- 78. Z. El Adnani, M. Mcharfi, M. Sfaira, M. Benzakour, A. T. Benjelloun, M. Ebn Touhami, DFT theoretical study of 7-R-3methylquinoxalin-2(1H)-thiones (Rdouble bond; length as m-dashH; CH₃; Cl) as corrosion inhibitors in hydrochloric acid, Corros. Sci., 68 (2013) 223-230.
- **79.** R. G. Pearson, Absolute electronegativity and hardness correlated with molecular orbital theory, Proc. Nati. Acad. Sci., 83 (1986) 8440-8441.
- R. G. Parr, L. V. Szentpaly, S. Liu, Electrophilicity Index, J. Am. Chem. Soc., 121 (1999) 1922-1924.
- **81.** I. Lukovits, E. Kalman, F. Zucchi, Corrosion inhibitors—correlation between electronic structure and efficiency, Corros., 57 (2001) 3-8.
- F. Weinhold, C. Landis, Valency and Bonding, A Natural Bond Orbital Donor Acceptor Perspective; Cambridge University Press: Cambridge, U.K., 2005.
- 83. S. E. Nataraja, T. V. Venkatesha, H.C. Tandon, Computational and experimental evaluation of the acid corrosion inhibition of steel by tacrine, Corros. Sci., 60 (2012) 214–223.
- 84. G. Bereket, E. Hur, C. Ogretir, Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium, j. Mol. Struct., 578 (2002) 79-88.

- **85.** R. G. Pearson, Absolute electronegativity and hardness: application to inorganic chemistry, Inorg. Chem., 27 (1988) 734-740.
- **86.** V. S. Sastri, J. R. Perumareddi, Molecular orbital theoretical studies of some organic corrosion inhibitors, Corros., 53 (1997) 617-622.
- 87. M. J. S. Dewar, W. Thiel, Ground States of Molecules, 38. The MNDO Method. Approximations and Parameters, J. Am. Chem. Soc., 99 (1977) 4899-4907.
- 88. B. Gomez, N. V. Likhanova, M. A. Dominguez-Aguilar, R. Martinez-palou, A. Vela, J. Gazquez, Solvent Triggered Change of the Electron Excitation Route of KI in Supercritical NH₃, J. Phy. Chem. B., 110 (2006) 8928-8934.
- 89. T. Arslan, F. Kandemirli, E. E. Ebenso, I. Love, H. Alemu, Quantum chemical studies on the corrosion inhibition of some sulphonamides on mild steel in acidic medium, Corros. Sci., 51 (2009) 35–47.
- **90.** S. Noorizadeh, H. Maihami, A theoretical study on the regioselectivity of Diels– Alder reactions using electrophilicity index, J. Mol. Struct., 763 (2006) 133-144.
- **91.** K. Emregul, E. Duzgun, O. Atakol, The application of some polydentate Schiff base compounds containing aminic nitrogens as corrosion inhibitors for mild steel in acidic media, Corros. Sci., 48 (2006) 3243-3260.
- 92. L. Vera, M. Guzman, P. Ortega-Luoni, QSPR Study of corrosion inhibitors. imidazolines, J. Chil. Chi. Soc., 51 (2006) 1034-1035.
- 93. M. Touil, N. Hajjaji, D. Sundholm, H., Rabaâ, Computational studies of the corrosion-inhibition efficiency of iron by triazole surfactants, Int. J. Quantum. Chem., 113 (2013) 1365-1371.
- **94.** I. Lukovits, A. Shaban, E. Kalman, Corrosion inhibitors: quantitative structure– activity relationships, Russian J. Electrochem., 39 (2003) 177-181.

LIST OF TABLE

No.	Caption								
	Surface-active properties of the synthesized Schiff base gemini surfactant compounds								
IABLE I	(SBGS-10, SBGS-14 and SBGS-16).								
	Electrochemical impedance parameters (mean and relative standard deviation n=3)								
TABLE 2	for mild steel in 1.0 M H ₂ SO ₄ without and with various concentrations of the								
	synthesized Schiff base gemini surfactants at 50 °C								
	Electrochemical parameters (mean and relative standard deviation n=3) obtained								
TABLE 3	from polarization measurements for mild steel in 1.0 M H_2SO_4 without and with								
	different concentrations of SBGS inhibitors at 323 K.								
TABLE A	Adsorption isotherm models and their regression coefficients (R^2) for SBGS								
TADLE 4	inhibitors on mild steel in 1.0 M H_2SO_4 at 323 K								
	The calculated quantum chemical parameters of the studied inhibitors SBGS-10,								
TABLE 5	SBGS-14 and SBGS-16 in the neutral form obtained using DFT at the B3LYP/6-								
	31G(d,p) basis set in the gas and water media.								
	N -								

<u>Table 1:</u>

Compounds	CMC ^a / mM L ⁻¹	CMC ^b / mM L ⁻¹	CMC ^c / mM L ⁻¹	γсмс/ mN m ⁻¹	$\pi_{\rm CMC}$ / mN m ⁻¹	α	β	Γ _{max} / mol/cm ⁻²	$A_{\min}/$ nm ²	$\Delta G_{ m mic}^{ m o}$ / kJ mol ⁻¹	$\Delta G_{ m ads}^{ m o}$ / kJ mol ⁻¹
SBGS-10	0.458	0.401	0.450	37.38	34.62	0.45	0.55	3.65 ×10 ⁻¹⁰	0.45	-29.52	-30.45
SBGS-14	0.440	0.388	0.445	36.82	35.18	0.50	0.50	3.40×10^{-10}	0.49	-28.72	-29.75
SBGS-16	0.399	0.376	0.379	35.73	36.27	0.68	0.32	3.25 ×10 ⁻¹⁰	0.51	-25.59	-26.70

^a CMC values obtained from surface tension measurements in water.

^b CMC values obtained from surface tension measurements in 1.0 H_2SO_4 .

^cCMC values obtained from conductivity measurements.

Table 2:

Inhibitors C		P /	$R_{\rm ct}$		D (D /	I/	Q _{CPE}			
code	∪ _{inh/} mM	$\Omega \text{ cm}^2$	$\Omega \text{ cm}^2 \pm \text{SD}$	$\mu F cm^{-2}$	$\Omega \text{ cm}^2$	$\Omega \text{ cm}^2$	H cm ²	$\frac{Y_0}{\mu \Omega^{-1} s^n}$	n	θ	P _{EIS} /%
Blank	0.0	0.43	7.1±0.5	850	6.4	64.9	4.7	68.65	0.795		
	0.01	0.45	19.5±1.3	309	16.4	103.1	13.11	24.72	0.897	0.635	63.58
	0.05	0.48	24.1±2.1	250	20.7	146.7	16.21	20.23	0.907	0.705	70.53
SBGS-10	0.10	0.50	42.9±3.4	140	37.3	285.7	28.94	11.24	0.918	0.834	83.45
	0.50	0.63	65.2±5.7	92	56.6	429.1	44.05	7.36	0.928	0.891	89.11
	1.00	0.96	105.6±8.3	57	92.1	720.4	71.12	4.56	0.938	0.932	93.27
	0.01	0.44	24.7±1.9	244	21.3	154.7	16.61	19.52	0.907	0.712	71.25
	0.05	0.51	29.6±2.3	203	25.8	200.9	19.92	16.24	0.897	0.760	76.01
SBGS-14	0.10	0.62	47.1±4.2	128	40.4	284.1	31.66	10.24	0.918	0.849	84.92
	0.50	0.65	88.2±6.5	68	78.1	682.2	59.61	5.44	0.928	0.919	91.95
	1.00	1.10	146.6±12.8	41	125.9	891.6	98.84	3.28	0.948	0.951	95.15
	0.01	0.51	32.7±2.6	184	29.2	272.8	22.02	14.72	0.928	0.782	78.28
	0.05	0.57	47.8±3.8	126	43.2	448.9	32.16	10.08	0.938	0.851	85.14
SBGS-16	0.10	0.70	58.4±4.3	103	53.0	573.1	39.34	8.24	0.928	0.878	87.84
	0.50	1.28	107.5±8.7	56	94.5	781.4	72.37	4.48	0.969	0.933	93.39
	1.00	2.09	199.6±16.1	30	173.8	1344.5	135.09	2.42	0.973	0.964	96.44
		•			•	•	•				
			\mathbf{C}								
		C									
		X	-								

Table 3:

Inhibitors code	C _{inh} / mM	J _{corr} / μAcm ⁻² ±SD	-E _{corr} / mV (SCE) ±SD	β _a / mV dec ⁻¹ ±SD	-β _c / mV dec ⁻¹ ±SD	θ	P _{PDP} / %	P _{cal} /% From Eq. 25	P _{cal} /% From Eq. 26
Blank	0.0	794±56	471 ±6	126±11	225±18		-	-	
	0.01	268.76±21.3	476±4	72±6	199±15	0.661	66.15	91.76	90.48
	0.05	217.47±17.5	474±5	71±5	212±13	0.726	72.61	98.24	97.94
SBGS-10	0.10	107.51±7.4	467±3	70±4	215±17	0.864	86.46	99.11	98.95
	0.50	50.34±4.1	451±6	71±6	190±12	0.936	93.66	99.82	99.79
	1.00	16.04±1.3	452±2	73±4	207±11	0.979	97.98	99.91	99.89
	0.01	234.15±23.1	454±5	72±8	214±19	0.705	70.51	91.94	90.72
SBGS-14	0.05	165.78±15.7	464±4	75±4	208±20	0.791	79.12	98.28	97.99
	0.10	69.71±5.2	480±3	71±6	201±15	0.912	91.22	99.13	98.98
	0.50	27.31±1.7	471±3	72±5	203±12	0.965	96.56	99.82	99.79
	1.00	13.34±0.8	459±5	74±6	207±10	0.983	98.32	99.91	99.89
	0.01	204.53±19.8	480±5	71±4	216±15	0.742	74.24	92.02	90.82
	0.05	127.35±11.2	459±4	72±8	198±10	0.839	83.96	98.30	97.02
SBGS-16	0.10	46.45±3.5	457±6	70±8	208±9	0.942	94.15	99.14	99.00
	0.50	14.13±1.2	465±2	71±5	210±8	0.982	98.22	99.83	99.79
	1.00	6.27±0.52	466±4	72±6	214±14	0.992	99.21	99.91	99.89
		× ·							

Table 4:

Adsorption			
isotherms	8BG8-10	8BG8-14	SBGS-10
Flory-Huggins	0.93915	0.92012	0.94124
Langmuir	0.99976	0.99996	0.99999
Frumkin	0.91231	0.88774	0.87991
Temkin	0.89764	0.89891	0.88996
Freundlich	0.95113	0.94326	0.96113

Table 5:

Quantum		Gas medium	1	Water medium				
chemical	SBGS -10	SBGS-14	SBGS-16	SBGS -10	SBGS-14	SBGS-16		
parameters	Model	Model	Model	Model	Model	Model		
E _{total} / au	-2893.67	-3208.20	-3365.47	-2893.70	-3208.23	-3365.50		
<a>	492.33	583.40	628.82	616.46	728.79	784.93		
$\mu_{ m potential}$ / eV	-4.541	-4.536	-4.536	-4.659	-4.657	-4.657		
$I_{\rm p}/({\rm eV})$	5.30	5.29	5.29	5.814	5.810	5.810		
$\mu_{ ext{dipole}}$ / Debye	8.96	9.03	9.03	11.44	11.51	11.51		
$E_{ m HOMO}$ / eV	-5.30	-5.29	-5.29	-5.814	-5.810	-5.810		
$E_{ m LUMO}$ / eV	-3.781	-3.782	-3.782	-3.505	-3.505	-3.505		
$\Delta E/ \mathrm{eV}$	1.519	1.508	1.508	2.309	2.305	2.305		
η/ eV	0.760	0.754	0.754	1.154	1.152	1.152		
σ / eV ⁻¹	1.317	1.326	1.326	0.866	0.868	0.868		
χ/ eV	4.541	4.536	4.536	4.659	4.657	4.657		
$E_{ m A}$ / eV	3.781	3.782	3.782	3.505	3.505	3.505		
ω/eV	7.83	7.75	7.75	9.403	9.410	9.410		
$\Delta E_{ m Back-donation}$	-0.189	-0.188	-0.188	-0.289	-0.288	-0.288		
ΔN	2.53	2.54	2.54	-1.013	-1.016	-1.016		
P _{PDP} /% ^a	97.98	98.32	99.21	97.98	98.32	99.21		
$P_{\rm cal}$ /% ^b	99.91	99.91	99.91	99.89	99.89	99.89		

^a P_{PDP} /% : Inhibition efficiency obtained from potentiodynamic polarization measurements

^b P_{cal} /%: Calculated inhibition efficiencies of the inhibitors obtained using equations 25, 26, 27 and 28 for gas and water medium, respectively.

LIST OF FIGURES

No.	Caption							
F ¹ 1	General Scheme for the preparation of the three Schiff base gemini surfactants (SBGS-							
Figure 1	10, SBGS-14 and SBGS-16).							
	FT-IR (a) ¹ H-NMR (b) and ¹³ C-NMR (c) spectra of 3,3'-(pentane-2,4-							
Figure 2	diylidenebis(azanylylidene))bis(N,N-dimethyl-N-(2-(hexadecyloxy)-2-							
	oxoethyl)propan-1-aminium) chloride [SBGS-16].							
Figure 3	Variation of the surface tension with the concentration of the prepared Schiff base							
rigure 5	gemini surfactants in (a) water and (b) 1.0 M H ₂ SO ₄ at 298 K.							
Figure 4	Plotting of specific conductivity against concentration of the Schiff base gemini							
i iguite i	surfactants in water at 298 K.							
Figure 5	Variation of biodegradation (%) with time (day) for the synthesized Schiff base gemini							
Figure 5	surfactants.							
	Open circuit potential (E_{corr})-time curves of mild steel immersed in 1.0 M H ₂ SO ₄							
Figure 6	solution in the absence and presence of 1.0 mM of synthesized SBGS inhibitors at 50							
	°C.							
	Nyquist (a , c and e) and Bode and phase modules (b , d and f) plots for mild steel in							
	1.0 M H_2SO_4 in the absence and presence of various concentrations of the							
Figure 7	synthesized SBGS-10, SBGS-14 and SBGS-16 inhibitors, measured at E_{corr} , Ac							
	amplitude 10 mV, the frequencies from 100 kHz to 0.5 Hz and at 50 °C. Symbols							
	(■ ◄) Experimental; Line (—) Simulated.							
Figuro 8	EIS fitting curves and their corresponding equivalent circuit for mild steel in the							
riguit o	absence (a) and presence (b) of 1.0 mM SBGS-14.							
Figure 9	Potentiodynamic polarization curves for mild steel in 1.0 M H ₂ SO ₄ solution without							

	and with different concentrations of (a) SBGS-10, (b) SBGS-14 and (c) SBGS-16 at
	323 K.
FI 10	Langmuir adsorption isotherm for SBGS-10, SBGS-14 and SBGS-16 on mild steel in
Figure 10	1.0 M H ₂ SO ₄ at 323 K. Experimental data (points) and Linear fit of data (red lines)
	SEM micrographs for mild steel after immersion in 1.0 M H_2SO_4 for 3 days in (a)
Figure 11	absence and presence of (b) 1.0 mM of SBGS-10, (c) 1.0 mM of SBGS-14 and (d) 1.0
	mM of SBGS-16.
Eiguno 12	Optimized structures and frontier molecular orbitals (HOMO and LUMO) for the
rigure 12	studied SBGS compounds, (a) SBGS-10, (b) SBGS-14 and (c) SBGS-16
	Natural atomic charges from natural bond orbital analysis (NBO) calculated at
Figure 13	B3LYP/6-31G (d,p) basis set for the studied surfactants (a) SBGS-10, (b) SBGS-14
	and (c) SBGS-16.
D ² 14	Molecular electrostatic potential map (MEP) of inhibitors (a) SBGS-10, (b) SBGS-14
Figure 14	and (c) SBGS-16.











<u>Figure 5</u>



<u>Figure 6</u>





<u>Figure 8</u>















Graphical abstract

Novel Synthesized Schiff Base- based Cationic Gemini Surfactants: electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion

Hany M. Abd El-Lateef^{a, b}*, Kamal A. Soliman^c, Ahmed H. Tantawy^c

^a Department of Chemistry, College of Science, King Faisal University, Al Hufuf, 31982 Al Hassa, Saudi Arabia

^bChemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt ^c Chemistry Department, Faculty of science, Benha University, 13518Benha, Egypt

E-mail address: <u>Hany_shubra@yahoo.co.uk</u> (Hany M. Abd El-Lateef)



<u>Highlights</u>

- Three novel Schiff Base surfactants have been successfully synthesized.
- All synthesized surfactants inhibit mild steel corrosion in 1.0 M H₂SO₄.
- The adsorption model obeys to the Langmuir isotherm.

- Potentiodynamic polarization studies showed that the studied surfactants are mixed-type inhibitors.
- The results obtained from theoretical calculations support our experimental studies.