# Inhibitory Effect of Some Cationic Gemini Surfactants for Carbon Steel in Sea Water

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**Abstract**   Corrosion inhibition of carbon steel alloy in sea water by different synthesized gemini surfactants {12-2-12, 14-2-14 and 16-2-16} have been investigated using weight loss, potentiodynamic polarization and surface tension measurements. The data obtained from all the used methods are in good agreement with each other and ensure the excellent inhibition efficiency of the tested surfactants for carbon steel in sea water. The inhibition efficiency increases with increasing the concentration of the studied inhibitors. Also, the adsorption ability of the surfactant molecules on carbon steel surface increases with the increase in the hydrocarbon chain length of the surfactant molecule from 12 to 16 and through 14 C atoms; meanwhile, the isotherm of 16-2-16 declares the formation of multilayer onto the used metal surface. The inhibitive action of the studied surfactants follows the order: 16-2-16 > 14-2-14> 12-2-12. The morphological changes of carbon steel surface were studied by Scanning Electron Microscope [SEM] ] and the study shows well inhibited surface on adding the cationic Gemini surfactants to the immersion solution  .

## 1. Introduction:

Low carbon steel is being used extensively under different conditions in industries because of its low cost and excellent mechanical properties. However, some corrosion problems take place due to the use of natural sea water in cooling systems, storage reservoirs, and water transport pipelines for injection systems [1]. In order to reduce the corrosion of metal, several techniques have been applied, where among that utilization of organic compounds and more specifically cationic surfactants are gaining high space as corrosion inhibitors. Surfactants are very beneficial reagents and their presence at very low quantity in any medium providing desirable properties to processes in all industries such as, petrochemical, food, paint and coating industry [2]. As a new generation of surfactants, gemini surfactants have attracted great interest in recent years. This kind of surfactant contains two hydrophilic groups and two hydrophobic groups in the molecule, separated by a rigid or flexible spacer, rather than one hydrophilic group and one hydrophobic group for conventional surfactants [3]. Gemini surfactants are about 3 orders of magnitude more efficient at reducing surface tension and more than 2 orders of magnitude more efficient at forming micelles than conventional surfactants [4]. Many gemini surfactants have been synthesized, and a considerable number of investigations have been reported on their unusual physicochemical properties, including their high surface activity, unusual changes
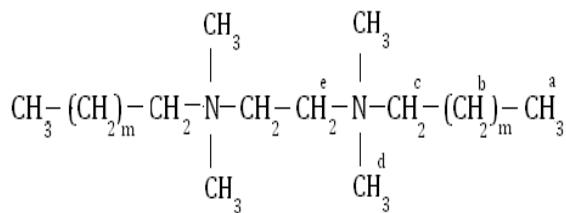
of viscosity, unusual micelle structure, and aberrant aggregation behaviors [5-13]. In general, cationic surfactants and particularly gemini surfactant possessing effective inhibitory effect, they accumulate in special order at the interfaces and modify the interfaces and thus, control, reduce, or prevent reactions between a substrate and its surroundings when added to the medium in small quantities [14].

In the present study, a series of gemini cationic surfactants with different chain lengths n-2-n (n = 12, 14, and 16 C atoms) are synthesized, purified, and characterized. Surface tension, weight loss, potentiodynamic polarization measurements, and scanning electron microscopy (SEM) were performed to examine the structural inhibitive effect of these tested inhibitors on the corrosion process of carbon steel in natural sea water. The adsorption mechanism of the gemini surfactants onto the carbon steel surface is discussed in order to shed light on the inhibition mechanism of the tested inhibitors.

## 2. Material and Methods
### 2.1. Synthesis

A series of cationic gemini surfactants N-alkanediyl 1, 2-ethane bis (dimethyl ammonium bromide) namely: 12-2-12, 14-2-14, and 16-2-16 were synthesized, then purified, and characterized. The structure is shown in the following scheme

**Molecular structure of the studied Gemini surfactant**

where m= 10, 12, or 14

The tested surfactants were prepared from N, N, N', N'-tetramethylethylene diamine and the corresponding alkyl bromides of n = 12, 14, and 16 in absolute ethanol under reflux for 24 hours. Ethanol is removed via rotary evaporator where a waxy product was obtained. The resulting product was extracted, using diethyl ether and recrystallized from acetone/ethyl acetate mixture [15].The chemical structure of the prepared surfactants was confirmed by the following techniques:

**a) Elemental analysis**
        Elemental analyses were performed for the prepared surfactants via Elemental Analyzer Perkin Elmer 240 C, and the obtained results are given in Table (1).

**b) $^1$H-NMR**
        $^1$H-NMR for the prepared surfactants was measured using Jeol-EX-270 MHz NMR Spectrophotometer. The following bands were shown (MHz, δ, CDCl$_3$/TMS): (a) t, 0 .87 ppm; (b) m, 1.23 ppm; (c) m, 1.79 ppm; (d) s, 3.14 ppm; (e) m, 3.55 ppm.

**c) Mass spectra**
        The prepared surfactants were analyzed via mass spectra using GC Mass-Qt 1000 EX Schimatz Spectrophotometer, Japan E.I. 70 EV. The giving data were:

**12-2-12:** (m/z = 613.8; $[M+ 1-^{81}Br]^+$ = 533.4; $[M-2Br/2]^+$ = 226
**14-2-14:** (m/z = 669.8; $[M+ 1-^{81}Br]^+$ = 593.5; $[M-2Br/2]^+$ = 254.1
**16-2-16:** (m/z = 725.8; $[M+ 1-^{81}Br]^+$ = 675.5; $[M-2Br/2]^+$ = 332.1

**2.2. Solution**
        The sea water used in this study was collected from Mediterranean Sea (Alexandria-.Egypt). Its constituents were defined by Atomic absorption spectroscopy ( AAS) technique and the obtained results are given in Table (2).

**2.3. Surface Tension measurements**
        The surface tension at air/liquid interface of the tested surfactants was measured in sea water solution of different concentrations (2.0 x $10^{-5}$- 6.0 x $10^{-3}$ mol dm$^{-3}$) by Krüss Tensiometer K 6 at 25°C using the Platinum ring method.

**2.4. Adsorption Measurements**
        The adsorption isotherms of the tested surfactants onto carbon steel surface were obtained by the immersion method (at 25 °C). Coupons, of the used metal, were equilibrated for 144 hours in 25 ml of surfactant solutions of known concentrations ranged from 2.0 x $10^{-5}$ mol dm$^{-3}$ to   6.0 x $10^{-3}$ mol dm$^{-3}$. The amount adsorbed was calculated from the changes in concentration of the solutions using the curves given in Fig. 1 as a calibration curve, according to the following equation,

$$\Gamma = \frac{(C_o - C_{eq})V}{m} \qquad (1)$$

where $\Gamma$ is the amount adsorbed in m mol g$^{-1}$, C  is the initial surface concentration in m mol dm$^{-3}$; $C_{eq}$ is the surfactant concentration at equilibrium in m mol dm$^{-3}$; V is the volume of the liquid phase in liter; and m is the mass of adsorbent in gram.

**2.5. Gravimetric Measurements**
        Rectangular specimens of low carbon steel (2.5cm × 2.0 cm ×0.5 cm) were abraded with 180, 400, 600, and 1200 grades of emery paper they were degreased with acetone and rinsed with distilled water two times. Then, they were immersed in 0.5 M HCl solution for 10 sec, rinsed with distilled water two times and finally dried. The specimens were accurately weighted and then immersed in 25cm$^3$ of sea water with and without different concentrations of the studied surfactants. After 144 hrs, the steel sheets were taken out, rinsed thoroughly with distilled water, dried, and reweighted accurately. The weight loss of the carbon steel sheets was obtained. .The chemical composition of the used carbon steel sheets is listed in Table (3).

**2.6. Electrochemical Measurements**
        Electrochemical experiments were carried out using Potentiostat Galvanostat (EG & G model 273). Standard ASTM glass electrochemical cell was used. Platinum electrode was used as auxiliary electrode .All potentials were measured against saturated calomel electrode (SCE) as a reference electrode. The working electrode has a form of square with a surface area of 2.25 cm$^2$. All experiments were conducted at room temperature. Potentiodynamic

polarization curves were obtained by changing the electrode potential automatically from -1000 to +1000 mV with a scan rate 10 mvs$^{-1}$.

### 2.7. Scanning Electron Microscopy (SEM)

The surface examination of carbon steel samples in sea water, without and with the optimum concentration of tested inhibitors was performed using scanning electron microscope (Jeol 5400). The energy of the acceleration beam employed was 30 KV.

## 3. Results and Discussion
### 3.1. Surface properties

The surface tension values ($\gamma$, mNm$^{-1}$) for the cationic gemini surfactants under investigation were plotted against the logarithm of the surfactant concentration (Log C, mol dm$^{-3}$) as shown in Fig. 1 (a, b and c) for 12-2-12, 14-2-14 and 16-2-16, respectively. The critical micelle concentrations (CMCs) of the tested surfactants were determined from the point of intercept of the two linear portions obtained by the $\gamma$-Log C plots.

It is clear that, for all the tested cationic gemini surfactants, the surface tension decreases with increasing the concentration until CMC is reached, above which the surface tension is not affected by a further increase in the surfactant concentration.

The obtained CMC values for the studied surfactants are reported in Table (4). The surface excess concentration $\Gamma_{max}$ (in Mol cm$^{-2}$) and the surface area per molecule $A_{min}$ (in nm$^2$) for the investigated surfactants were calculated according to the following equations [16]

$$\Gamma_{max} = -1/nRT \ (\partial \gamma / \partial \ln C)_{T,P} \qquad (2)$$

where n=3 for ionic gemini surfactants

$$A_{min} = 10^{-14}/N_A \ \Gamma_{max} \qquad (3)$$

where $N_A$ is the Avogadro's number. The obtained data is reported in Table (4).

It is observed that the surface value of $A_{min}$ increases with increasing the hydrophobic chain length of the tested surfactants. This is because $A_{min}$ depends primarily on the adsorption interface which is, in turn, affected by the total number of carbon atoms in the chain and hence on the hydrophobicity of the surfactant [17].

### 3.2. Adsorption of the tested surfactants onto carbon mild steel surface

The efficiency of an inhibitor in inhibiting the metal corrosion depends on the extent to which this inhibitor adsorbs onto that metal surface and the configuration in which they adsorb. So, measurements of adsorption isotherms can lead to a better understanding of the corrosion inhibition behavior of the tested surfactants. The amount of surfactant adsorbed onto the tested carbon mild steel surface, $\Gamma$ in m mol g$^{-1}$, has been determined as a function of surfactant concentration and plotted against the surfactant equilibrium concentration $C_{eq}$ (in m mol dm$^{-3}$) at 25ºC as shown in Fig 2 (a, b, and c) for the tested gemini surfactants 12-2-12, 14-2-14 and 16-2-16, respectively.

The adsorption isotherms of all the investigated cationic gemini surfactants exhibit segmoidal S-shapes as shown in Fig (2). The formation of multilayer onto the adsorbent surface represents a strong interaction between the adsorbed molecules themselves whereby cooperative adsorption occurs in the hydrocarbon chains [18].

Close looking at the isotherm of 12-2-12 illustrated in Fig 2 a displays the missing of the first horizontal region of the S-shape isotherm, this is attributed to the positive charge on the metal surface, which drives electrostatic repulsion that hinder adsorption of cationic surfactant [19]. This electrostatic repulsion is overcome in case of 14-2-14 & 16-2-16 due to the increase in the length of their hydrocarbon chains as illustrated in Fig 2 b & c where region I is clearly shown. This may be related to the increase in the hydrophobic properties of the surfactant molecule, which, in turn, increases its ability of forcing the surfactant molecules to adsorb onto the metal surface in order to improve the thermodynamic balance of the system. At the beginning of region I, in case of 14-2-14 & 16-2-16, and at low concentration below their CMCs, the adsorption is taken place at the cathodic charged surface sites result from the anions present in the used sea water (Table 2). The adsorption in this step is taken place by an electrostatic ion-exchange mechanism.

In spite of the presence of electrostatic repulsion, adsorption of the cationic gemini surfactant 12-2-12 onto the tested metal surface is taken place in region II. At the beginning of this region and at low concentration below CMC of the tested surfactant, the adsorption is taken place by an electrostatic ion-exchange mechanism. This result declares that the electrolytes present in the used sea water help the adsorption of this surfactant onto the investigated metal surface, which possesses +ve charged sites. This fact is in concomitance with that recorded by Rosen [20]. Also, Asefi et al. [21] deduced that the inhibition efficiency of gemini surfactants increases with the presence of halide salt. The head groups of the adsorbed molecules are firstly

oriented toward the metal surface while their hydrophobic tails lay horizontally or titled forming a monolayer onto the substrate. By increasing the surfactant concentration, surfactant molecules adsorb onto the metal surface by cooperative hydrophobic interactions of the oncoming surfactants ions with the already adsorbed molecules and with themselves. This aggregation is known as hemimicelle formation with the adsorbed molecules oriented perpendicularly toward the tested substrate where their head groups faced the bulk solution. At the end of region II, the metal surface has acquired a charge of the same sign as the surfactant ion. The adsorption in region III must overcome the electrostatic repulsion acting between the oncoming ions and the similarly charged solid, therefore, the slope of the isotherm in this region is reduced and the adsorption in case of 12-2-12 and 14-2-14 is leveled off when the surface is covered with the surfactant molecules (Figs. 2 a & b). This behavior is in line with that previously published [22].

The increase in the hydrophobic chain length from 14 C to 16 C leads to the increase in the slope of the isotherm as represented by region IV for the tested surfactant 16-2-16 (Fig. 2 c). This event may be attributed to the formation of multilayer or a sort of aggregation of the adsorbed molecules onto the used metal surface.

### 3.3. Weight loss tests

The weight loss tests are carried out in sea water in the presence of different concentrations of the tested surfactants (12-2-12, 14-2-14, and 16-2-16) at 25ºC. For all the investigated surfactants, a decrease in the weight loss of carbon steel in the presence of these additives is observed as general trend even at a low concentration compared with the surfactant free solution.

The corrosion rate $(K)$ was calculated using the following equation [23]:

$$K \quad = \quad W / St \qquad (4)$$

where W is the weight loss of the carbon steel sheets, S is the surface area of the specimen, and t is the immersion time. Also, the inhibition efficiency ($\eta_w\%$) and surface coverage ( ) were calculated according to the following equations [24] :

$$\eta_w\% \quad = \quad (W_{corr.} - W_{corr.(inh)} / W_{corr} \times 100 \quad (5)$$
$$= \quad (W_{corr.} - W_{corr.(inh)} / W_{corr.} \qquad (6)$$

where, $W_{corr.}$ and $W_{corr.(inh)}$ are the weight loss of carbon steel in absence and in presence of the inhibitors, respectively. The obtained weight loss data of the carbon steel in sea water and in presence

of various concentrations of inhibitors are recorded in Table (5). The results show that all the tested surfactants act as good corrosion inhibitors for carbon steel in sea water but with different extents. Also, the obtained data (Table 5) show an increase in the corrosion inhibition efficiency with the increase in the surfactant concentration.

Generally, it is agreed that the primary action in the inhibition process by surfactants is the adsorption of the surfactant molecules via their functional group onto the metal surface. As indicated from the data reported in Table (5), the higher the degree of the surface coverage the lower is the corrosion rate of carbon steel and hence the higher the inhibitor efficiency. This behavior is confirmed by the surface adsorption study for the used surfactants as shown in Figs. (2 a, b, and c). The trend presented by the adsorption isotherms given in this figure is in line with behavior shown in Fig.(3).

It is clearly evident from Table (5) and Fig.(3) that the cationic gemini surfactant 16-2-16 exhibits the highest extent of surface coverage among all the tested inhibitors, corresponding to the best inhibition effect. The value of ( ) in the presence of this surfactant approaches unity, indicating almost a full coverage of the surface with the adsorbed surfactant molecules. These appear to act as a good physical barrier shielding the corroding surface from the corrosive environment and thus bringing down the corrosion rate of carbon steel very significantly. As previously mentioned, this surfactant form a multilayer or sort of aggregation onto the tested metal surface (Fig. 2 c), which provides a good hydrophobic barrier against the corroded bulk solution.

On the basis of the view that corrosion inhibition by surfactants depends on the ability of these compounds to adsorb onto the corroding surface which is directly related to its capacity to aggregate to form clusters (micelles). The critical micelle concentration (CMC) can be considered as a key factor in determining the effectiveness of surfactants as corrosion inhibitors. It is well known that for a surfactant to be an excellent corrosion inhibitor it should exhibit a low CMC value, i.e., the inhibition effectiveness is inversely proportional to the CMC value [25]. This fact is clearly achieved fulfilled in this research where 16-2-16 exhibits the lowest CMC value among all the tested surfactants (Table 4) and possesses the highest efficiency in inhibit the tested metal surface against corrosion in sea water (Table 5).

The corrosion inhibition efficiencies for all tested surfactants, as shown in Fig (3), increase with increasing the hydrocarbon chain length following the order 16-2-16> 14-2-14 >12-2-12. This result

indicates that the adsorption ability of the investigated surfactants increases with the increase in the chain length of the surfactant molecule and hence improves its inhibitive action.

### 3.4. Potentiodynamic polarization measurements

Potentiodynamic polarization tests were performed on the carbon steel under investigation in the used sea water with and without the presence of different concentrations of tested surfactants. Fig.(4) illustrates an example of the anodic and cathodic polarisation curves measured in sea water with optimum concentration of the tested surfactant 16-2-16 since it showed the best performance. Also, the polarization curves with and without the addition of optimum concentration of 12-2-12 and 14-2-14 inhibitors are shown in Fig.(5). The typical Tafel polarization curves obtained for different concentrations of the investigated surfactants and blank show a change in shape of the cathodic and anodic curves.

Various corrosion parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and percentage of inhibition efficiency ($\eta_{pot}$ %) are given in Table (6). The corrosion current obtained for the tested carbon steel coupons in all surfactants solutions under investigation are lower than inhibitor free solution, i.e. blank. These lower corrosion current values for inhibitor solutions imply that the rate of electrochemical reactions are reduced due to the formation of a barrier layer over the carbon steel surface by the inhibitor molecules [26]. An increase in the inhibition efficiencies with the increase in the inhibitor concentration is observed in Table (6) for all the tested inhibitors where the highest value of inhibition efficiency ($\eta_{pot}$%) is observed at the surfactant concentration 6 m mol dm$^{-3}$ for all the tested surfactants. This result is in parallel with that obtained from the surface study where the adsorption isotherms given in Figs.(2 a, b, and c) for these surfactants show an increase in the adsorption with the increase in the surfactant concentration.

Weight loss and polarization results show that the tested surfactant 16-2-16 possesses the best inhibition action in comparison with all the tested surfactants and appears to create a good hydrophobic physical barrier to the aggressive ions, this barrier accounts for its high inhibition efficiency. This result is confirmed by the surface study where the adsorption isotherm illustrated in Fig 2 c for this surfactant demonstrates the formation of multilayer onto the used metal surface as previously discussed.

The data reported in Table (6) also reveals that $E_{corr}$ values of inhibited and uninhibited systems do not vary significantly indicating that both anodic and cathodic reaction are affected by the addition of the studied surfactants. This behavior leads us to suggesting that the studied cationic gemini surfactants are mixed type (anodic/cathodic) inhibitor [27, 28].

The good inhibitive action of the tested cationic gemini surfactants can be related to the fact that, quaternary ammonium salts have been used extensively as inhibitors against the corrosion of iron and steel, and this kind of organic molecules can be adsorbed on the metal surface because it can form a bond between the polar head groups and the metal surface thereby, reducing the corrosion attack on the metal surface [29].

It is known that the gemini surfactant molecule consists of two hydrophilic groups and two hydrophobic groups that results in a complicated adsorption of this kind of surfactants onto metal surfaces. As previously published [30], three different scenarios can exist for the monolayer adsorption of gemini surfactants onto the metal surface: (a) two hydrophilic ionic groups of gemini surfactant are adsorbed onto the metal surface site, (b) one hydrophilic group is adsorbed onto the surface site, while the other hydrophilic group is free in solution phase, and (c) both (a) and (b) co-exist. Visualization of the three sections is shown in Fig.(6). The first scenario (a) should be the main adsorption mechanism at low concentrations of gemini surfactants, and the gemini surfactant molecules tend to be adsorbed onto the steel surface at high concentrations according to the second scenario (b). But in fact, the third scenario should be more reasonable because of the interaction between molecules of gemini surfactant, which explains the increase in the inhibition efficiency accompanied with increasing the concentration of the tested surfactants.

### 3.5. Scanning electron microscopy (SEM)

Fig.(7-a) shows SEM image of carbon steel surface after immersion in sea water for 144 h in absence of inhibitor, while Figs.(7-b ,c and d) show SEM images of the steel specimen after immersion in sea water for the same time interval in presence of 6 m mol dm$^{-3}$ of , 12-2-12 ,14-2-14, and 16-2-16 surfactants, respectively. The resulting scanning electron micrographs reveal that the surface was strongly damaged in 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 (7-d ) shows smooth, well inhibited surface that confirms the good adsorption of 16-2-16 onto the used metal surface and, in turn, a high inhibition efficiency at this concentration.

## 4. Conclusions

1. All the studied cationic gemini surfactants exhibit S-shape adsorption isotherms with the formation of multilayer in case of 16-2-16.
2. Surface adsorption measurements, electrochemical studies, and weight loss measurements are in parallel to each other
3. The synthesized cationic gemini surfactants can be used as corrosion inhibitors for carbon steel   in sea water. Their inhibiting properties increase with increasing the hydrocarbon chain length   of the inhibitors according to order: 16-2-16 > 14-2-14 > 12-2-12.
4. Polarization measurements showed that the tested cationic gemini surfactants are mixed-type inhibitors.
5. The inhibition mechanism is attributed to the strong adsorption ability of the selected surfactants   on carbon steel surface, forming a good protective layer, which isolates the surface from the aggressive environment.

**Table ( 1 ) - The calculated and founded percentage values of C, H, and N for the tested gemini surfactants**.

| Elements  Surfactants | %C | | %H | | %N | |
|---|---|---|---|---|---|---|
| | Calculated | Found | Calculated | Found | Calculated | Found |
| 12-2-12 | 58.56 | 57.75 | 10.75 | 10.79 | 5.08 | 5.76 |
| 14-2-14 | 60.91 | 59.11 | 11.05 | 11.50 | 4.18 | 4.42 |
| 16-2-16 | 62.81 | 61.98 | 11.29 | 11.53 | 3.86 | 3.99 |

**Table (2) -Chemical composition of the used seawater**

| Element | $Fe^{2+}$ | $Li^+$ | $Na^+$ | $K^+$ | $S^{-2}$ | $Mg^{2+}$ | $Cl^-$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|
| Concentration (ppm) | 0.74 | 3066.00 | 12325.63 | 394.91 | 3066.00 | 137.91 | 21110.00 | 459.00 |

**Table ( 3 ) - Composition of  the used low carbon steel alloy.**

| Element | Fe | C | S | Mn | P |
|---|---|---|---|---|---|
| Wt % | 98.38 | 0.28 | 0.05 | 1.25 | 0.04 |

**Table  (٤)  -Critical  micelle  concentration  (CMC),  excess  surface  concentration  ($\Gamma_{max}$),  and minimum surface area ($A_{min}$) of the used cationic gemini surfactants**.
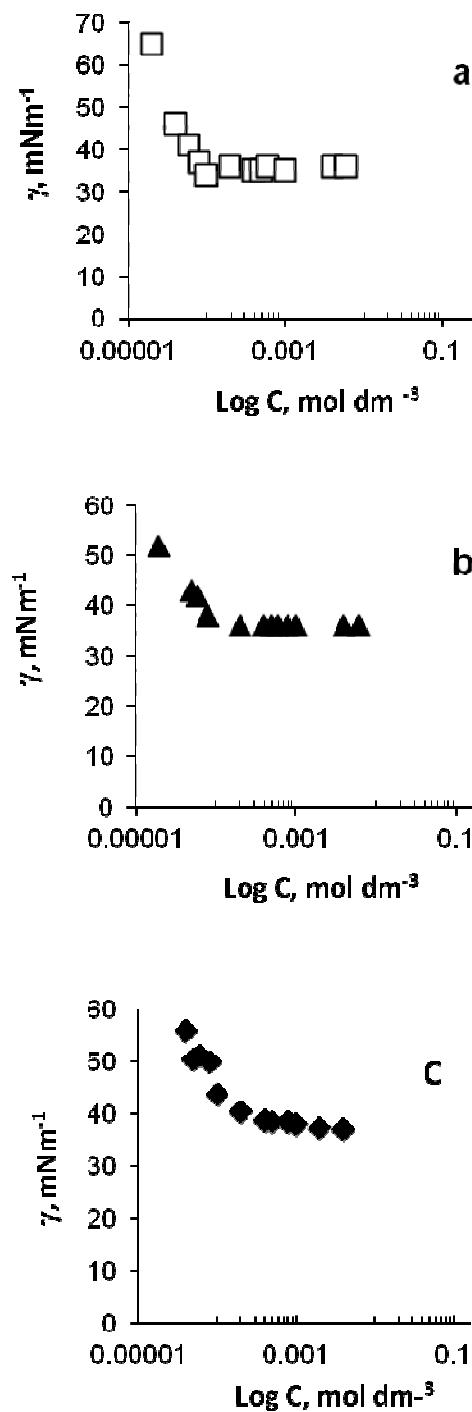
| Parameters | | | |
|---|---|---|---|
| Surfactants | CMC x $10^5$, mol $dm^{-3}$ | $\Gamma_{max}$ x $10^{10}$, Mol $cm^{-2}$ | $A_{min}$, $nm^2$ |
| 12-2-12 | 9.479 | 1.766 | 0.940 |
| 14-2-14 | 8.554 | 1.322 | 1.256 |
| 16-2-16 | 8.017 | 1.2578 | 1.78 |

**Table (5) - Corrosion Rate (*K*) of carbon steel, Surface Coverage ( ) and Corrosion inhibition Efficiency ($\eta_w$ %) (obtained from weight loss) in absence and presence of different concentrations of surfactants after 144 h immersion in sea water at 25 $^o$C .**
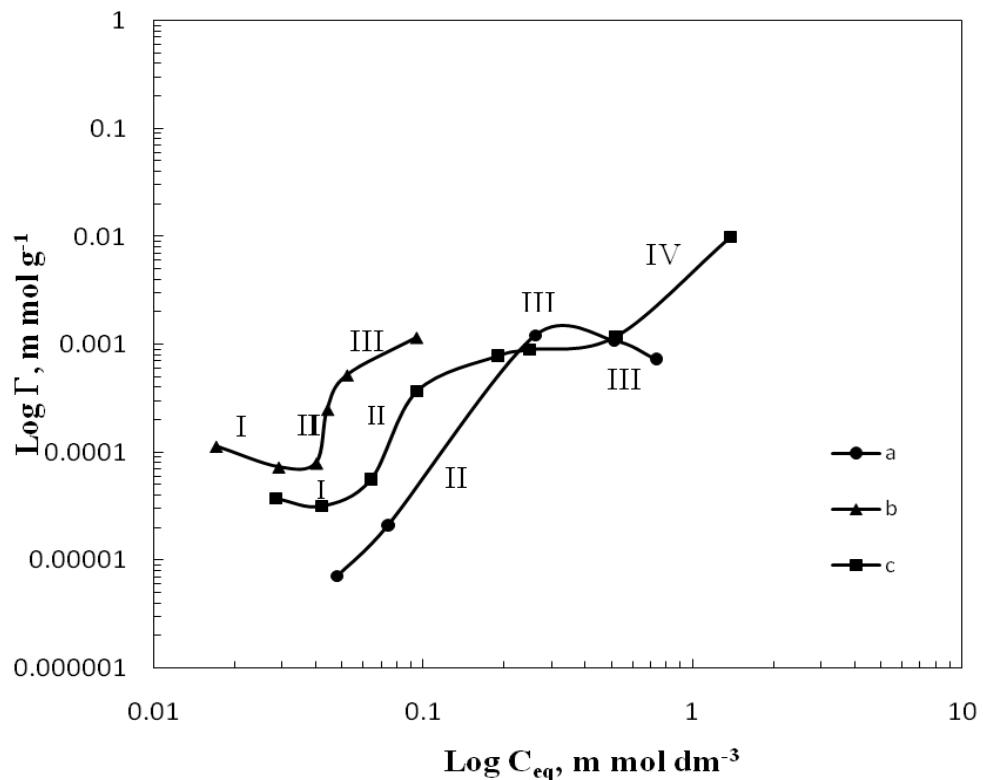
| Conc. m mol dm$^{-3}$ | $C_{12-2-12}$ | | | $C_{14-2-14}$ | | | $C_{16-2-16}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K$ mg cm h$^{-1}$ | | $\eta_w$% | $K$ mg cm h$^{-1}$ | | $\eta_w$% | $K$ mg cm h$^{-1}$ | | $\eta_w$% |
| 0.0 | 0.198 | - | - | 0.198 | - | - | 0.198 | - | - |
| 0.04 | 0.072 | 0.4555 | 45.55 | 0.062 | 0.5254 | 51.54 | 0.039 | 0.7098 | 79.08 |
| 0.06 | 0.059 | 0.5230 | 52.30 | 0.062 | 0.6514 | 65.14 | 0.030 | 0.8831 | 88.31 |
| 0.08 | 0.049 | 0.6692 | 66.92 | 0.051 | 0.7115 | 71.15 | 0.029 | 0.8923 | 89.23 |
| 0.4 | 0.040 | 0.6825 | 68.25 | 0.0398 | 0.7625 | 76.25 | 0.025 | 0.9083 | 90.83 |
| 0.6 | 0.038 | 0.6890 | 68.90 | 0.033 | 0.7975 | 79.75 | 0.018 | 0.9292 | 92.92 |
| 0.8 | 0.036 | 0.7335 | 73.35 | 0.029 | 0.8231 | 82.31 | 0.012 | 0.9315 | 93.15 |
| 2 | 0.033 | 0.8012 | 80.12 | 0.022 | 0.8960 | 89.60 | 0.009 | 0.9535 | 95.35 |
| 4 | 0.029 | 0.8820 | 88.20 | 0.0135 | 0.9315 | 93.15 | 0.008 | 0.9615 | 96.15 |
| 6 | 0.019 | 0.9395 | 93.95 | 0.0112 | 0.9545 | 95.45 | 0.001 | 0.9885 | 98.85 |

**Table (6) - Data obtained from potentiodynamic polarization measurements of carbon steel in sea water in absence and presence of various concentrations of the inhibitors at 25 $^o$C.**
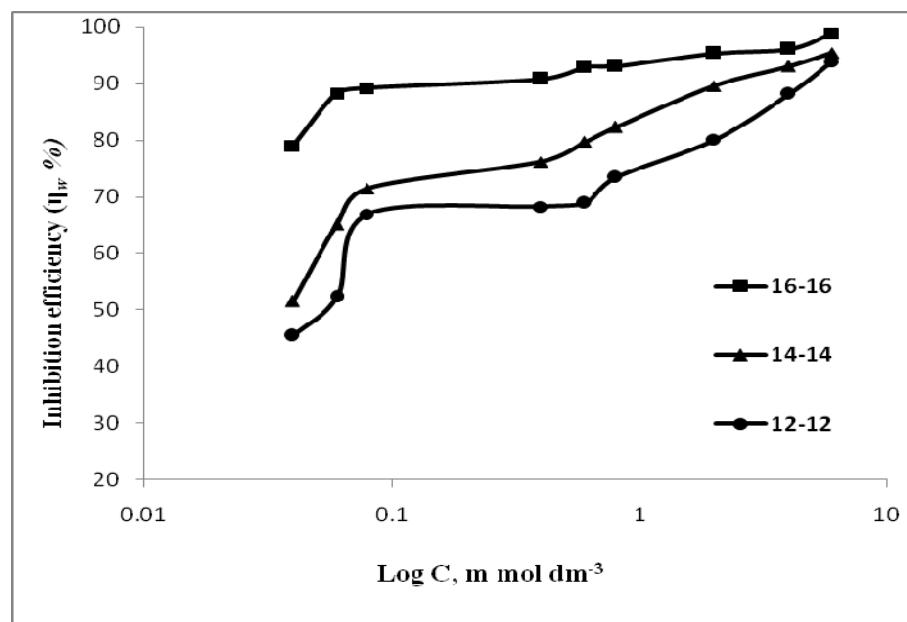
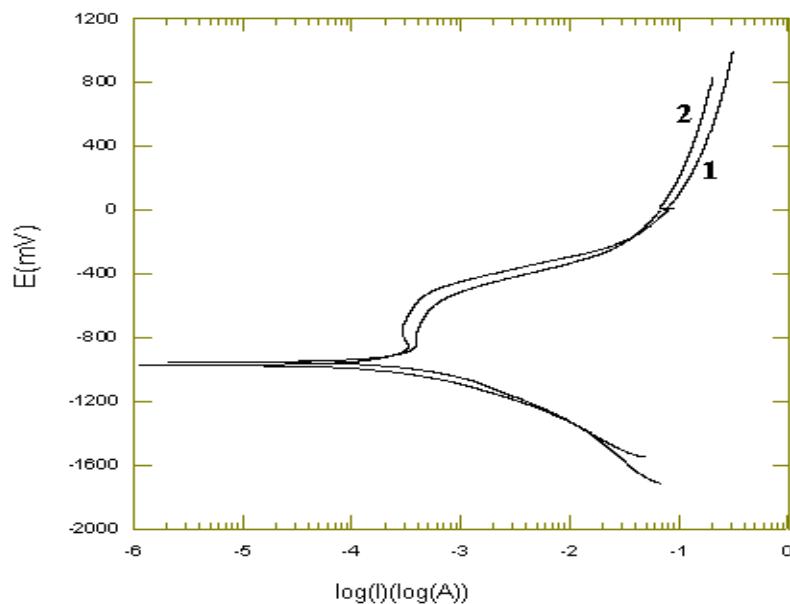| Conc. m mol dm$^{-3}$ | $C_{12-2-12}$ | | | $C_{14-2-14}$ | | | $C_{16-2-16}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E_{corr}$ (mV) | $i_{corr}$ (m A) | $\eta_{pot}$ (%) | $E_{corr}$ (mV) | $i_{corr}$ (m A) | $\eta_{pot}$ (%) | $E_{corr}$ (mV) | $i_{corr}$ (m A) | $\eta_{pot}$ (%) |
| 0.0 | -975 | 0.686 | - | -975 | 0.686 | - | -975.4 | 0.686 | - |
| 0.04 | -972 | 0.302 | 55.9 | -970 | 0.281 | 59.0 | -970 | 0.174 | 74.6 |
| 0.06 | -971 | 0.248 | 63.9 | -968 | 0.187 | 72.8 | -969 | 0.075 | 89.0 |
| 0.08 | -969 | 0.229 | 66.7 | -967 | 0.128 | 81.3 | -967 | 0.074 | 89.2 |
| 0.4 | -968 | 0.222 | 67.7 | -969 | 0.125 | 81.7 | -964 | 0.062 | 90.9 |
| 0.6 | -970 | 0.219 | 68.0 | -965 | 0.118 | 82.7 | -963 | 0.056 | 91.8 |
| 0.8 | -966 | 0.204 | 70.2 | -964 | 0.115 | 83.2 | -961 | 0.048 | 92.9 |
| 2 | -964 | 0.203 | 70.4 | -963 | 0.111 | 83.8 | -956 | 0.047 | 93.1 |
| 4 | -963 | 0.194 | 71.7 | -961 | 0.104 | 84.7 | -953 | 0.044 | 93.5 |
| 6 | -962 | 0.173 | 74.8 | -959 | 0.087 | 87.2 | -950 | 0.040 | 94.0 |

**Fig (1)- Surface tension vs log of molar surfactant concentration for the tested cationic gemini surfactants (a)12-2-12, (b) 14-2-14 and (c) 16-2-16.**
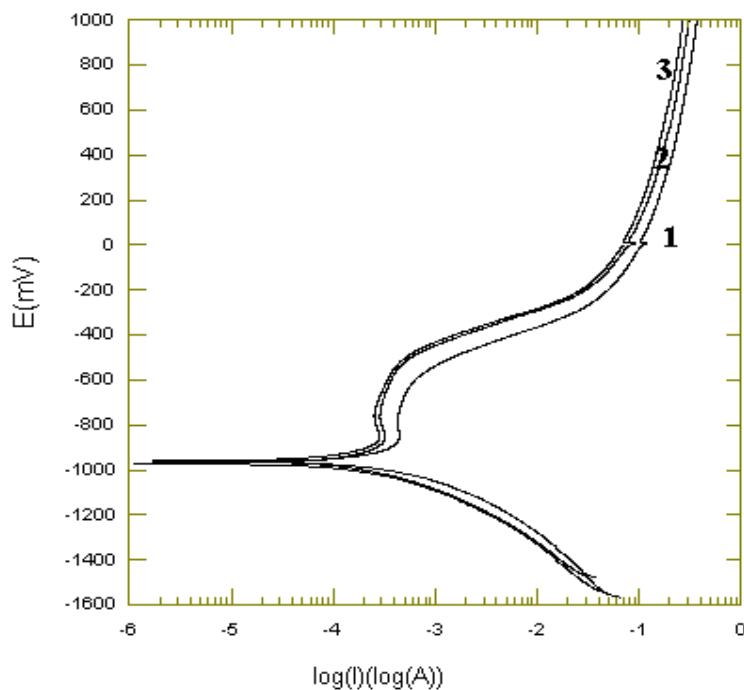
**Fig (2) – Adsorption isotherms of tested cationic Gemini surfactants from sea water onto carbon steel surface, (a) 12-2-12, (b) 14-2-14, (c) 16-2-16.**
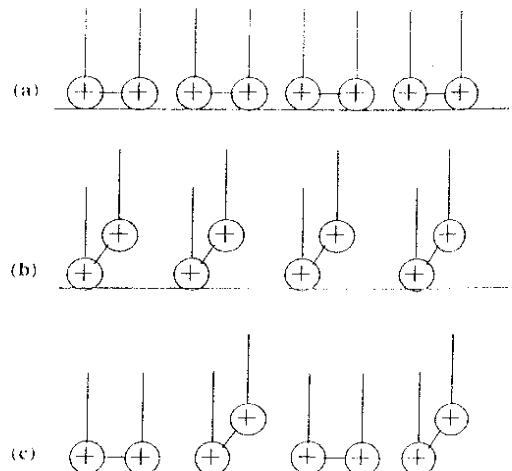


**Fig .(3)- inhibition efficiency of different tested surfactants (obtained from weight loss) as a function of surfactant concentration.**
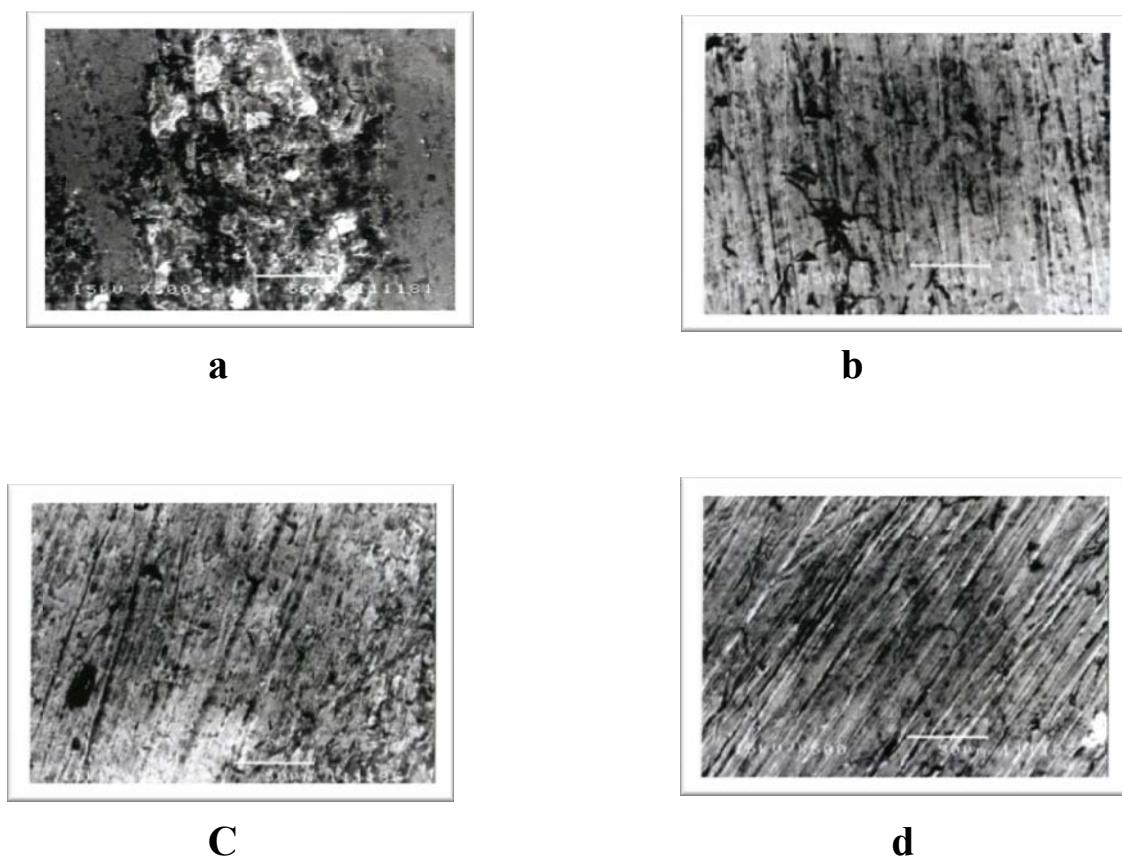
**Fig .(4)- Potentiodynamic    polarization curves of carbon steel in sea water ,(1) in absence of inhibitor ,(2) in presence of optimum concentration (6 m mol dm$^{-3}$) of 16-2-16 cationic gemini surfactant.**



**Fig.(5):Potentiodynamic polarization curves of carbon steel in seawater , (1)   in absence of inhibitor and in  presence of optimum concentration(6 m mol dm$^{-3}$) of (2)  12-2-12 and (3) 14-2-14 cationic gemini  surfactants.**

**Fig. (6) – Schematics for monolayer adsorption of Gemini surfactant onto carbon steel surface.**



**a**



**b**



**C**



**d**

**Fig. (7) – Scanning electron micrographs of carbon steel surface after immersion for 144 h in free inhibitor sea water (a) 12-2-12 (b) 14-2-14 (c) and 16-2-16 (d) gemini surfactants .**

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**References**

[1] Ghareba, S., and Omanovic, S., 2011. 12-Aminododecanoic acid as a corrosion inhibitor for carbon steel. Electrochimica., 15: 3890-3898.

[2] Shukla, D., and Tyagi, V.k., 2006. Cationic gemini surfactants: A Review. J.Oleo Sci., **55**: 381-390.

[3] Alejo, T., Merchán, M.D. and Velázquez, M.M., 2011. Specific ion effects on the properties of cationic Gemini surfactant monolayers. Thin Solid Films, **519**: 5689-5695

[4] Qiu, L.-G. , Xie, A. J. ,and Shen, Y. H., 2005. The adsorption and corrosion inhibition some cationic gemini surfactants on carbon steel surface in hydrochloric acid. Corros Sci., **47**: 273–278.

[5] Qiu, L.-G. , Xie, A. J., and Shen, Y. H., 2005. Understanding the effect of the spacer length on adsorption of gemini surfactants onto steel surface in acid medium. Appl. Surf. Sci., **246**: 1–5.

[6] Qiu, L.-G., Wang, Y. M. and Jiang X., 2008. Synergistic effect between cationic gemini surfactant and chloride ion for the corrosion inhibition of steel in sulphuric acid. Corr. Sci., **50** : 576–582.

[7] Qiu, L.-G. , Xie, A. J., and Shen, Y. H., 2004. Understanding the adsorption of cationic gemini surfactants on steel surface in hydrochloric acid. Mater. Chem. Phys., **87:** 237–240.

[8] Chen, Q., Zhang, D., Li, R., Liu, H. and Hu, Y., 2008. Effect of the spacer group on the behavior of the cationic gemini surfactant monolayer at the air/water interface. Thin Solid Films, **516**:8782-8787.

[9] Huang, W. and Zhao, J., 2006. Adsorption of quaternary ammonium gemini surfactants on zinc and the inhibitive effect on zinc corrosion in vitriolic solution. J. Coll. Surf. A, .**278**: 246– 251.

[10] Hegazy, M.A., 2009. A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution. Corrosion Science, 51: 2610–2618.

[11] Yu,D., Huang ,X., Deng ,M., and Lin,Y., 2010 .Effects of inorganic and organic salts on aggregation behavior of cationic gemini surfactants .J. Phys. Chem. B., **114** : 14955–14964

[12] Pei, X., Zhao, J., and Wei X., 2011. Wormlike micelles formed by mixed cationic and anionic gemini surfactants in aqueous solution. Journal of Colloid and Interface Science, 356: 176-181.

[13] Tehrani Bagha, A.R. , Bahrami, H., Movassagh, B., Arami, M., Arirshahi, S.H.,and Menger, F.M., 2007. Dynamic adsorption of gemini and conventional cationic surfactants onto Polyacrylonitrile. Coll. Surf. A., **307**: 121–127.

[14] Hegazy, M.A. , Abdallah,M., and Ahmed H. , 2010. Novel cationic gemini surfactants as corrosion inhibitors for carbon steel pipelines. Corr. Sci., **52**: 2897–2904.

[15] El Achouri, M., Infante, M.R., Izquierdo, Kertit, S., Gouttaya, H.M., and Nciri, B., 2001. Synthesis of some cationic gemini surfactants and their inhibitive effect on iron corrosion in hydrochloric acid medium. Corr.Sci., **43**: 19-35.

[16] Zana, R., and Xia, J., 2004. Gemini surfactants; synthesis, interfacial and solution-phase behavior, and applications", Surfactant Science Series Vol. 117, Marcel Dikker, Inc.; New York.

[17] Wang, W. and FreeM.L. , 2003. *Prediction and measurement of mild steel corrosion inhibition by alkyl pyridinium chloride and alkyl trimethyl ammonium bromide surfactants in acidic chloride media. Anti-Corrosion Methods and Materials,* **50**: 186.

[18] Giles, C.H., and Smith D. , 1974 . A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J. Colloid Interface Sci., **47** : 755.

[19] Atkin, R., Craig, V.S.J., Hartley, P.G., Wanless, E.J., and Biggs S. , 2003. Adsorption of ionic surfactants to a plasma polymer substrate Langmuir J, **19:** 4222-4227.

[20] Rosen, M.J., 1978.Surfactants and Interfacial Phenomena. 1st edn, John Wiley & Sons, New York.

[21] Asefi, D., Arami, M., and Mahmoodi, N.M., 2010. Electrochemical effect of cationic gemini surfactant and halide salts on corrosion inhibition of low carbon steel in acid medium.Corr. Sci., **52**: 794–800.

[22] Osman, M.M., and Shalaby, M.N., 2002. Some ethoxylated fatty acids as corrosion inhibitors for low carbon steel in formation water. Mat. Chem. and Phys., **77**: 261.

[23] Tang, L.B, Mu, G.N., and Liu, G.H., 2003. The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M hydrochloric acid .Corr. Sci., **45** : 2251.

[24] Vracar, L. M., and Drazic, D. M., 2002. Adsorption and corrosion inhibitive properties of some organic molecules on iron electrode in sulfuric acid. Corr. Sci., **44** : 1669 -1680.

[25] Migahed, M.A., Abd-El-Raouf , M.,. Al-Sabagh, A.M, and Abd-El-Bary H.M., 2005. Effectiveness of some non ionic surfactants as corrosion

inhibitors for carbon steel pipelines in oil fields. Electrochimica Acta , **50** : 4683–4689.

[26 ] Jacob, K. S. and Parameswaran, G., 2010. Corrosion inhibition of mild steel in hydrochloric acid solution by schiff base furoin thiosemicarbazone. Corr. Sci., **52** : 224-228.

[27] Quraishi, M.A., Jamal, D., and Luqman, M.,2002. Corrosion behaviour of VTS, STS and DTS inhibitors in formic and acetic acids. Indian J. Chem. Technol., **9**: 479–483.

[28] Sorkhabi, H.A., Shaabani, B. ,and Seifzadeh, D., 2005. Corrosion inhibition of mild steel by some schiff base compounds in hydrochloric acid. Appl. Surf. Sci., **239**: 154–164.

[29] Negm, N.A., Al Sabagh, A.M.,. Migahed, M. A, Abdel Bary, H.M. and El Din , H.M., 2010.Effectiveness of some diquaternary ammonium surfactants as corrosion inhibitors for carbon steel in 0.5 M HCl solution . Corr. Sci., **52**: 2122-2132.

[30] Qiu, L.-G. , Xie, A. J. and Shen, Y. H., 2005. A novel triazole-based cationic gemini surfactant: synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid Mater. Chem. Phys., **91**: 269-273.

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