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Phase transfer synthesis of novel based surfactants: Role of biocorrosion inhibition and corrosion of steel

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Abstract

Four novel aziridinium, pyrrolium and azepanium bis-quaternary ammonium salts joined within similarly aromatic spacer have been synthesized. The phase transfer synthesized cycloadduct as a selective and start-reaction material is a positive indicator for the corrosion inhibition process. The structures of the desired heterocyclic surfactants were confirmed by using elemental analysis, FT-IR and ^{1}H NMR spectral analysis. The adsorption of these compounds on the metal surface is found to obey Tafel adsorption isotherm. Furtheron, the dilution method need to be included to evaluate their biocorrosion inhibition. This study explores the corrosion resistance of the prepared bisquats in ^{1} M HCl and SRB corroded medium. The growth of the reference SRB (*Desulfomonas pigra*) was shown to be completely inhibited by bisquaternary ammonium surfactants, In1- In3, and also the inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing surface tension which is due to the fact, that the rate of corrosion of carbon steel is higher than the rate of adsorption and therefore indicates that the joint adsorption of these compounds and chloride ions by the addition of HCl is due to the increase of the surface coverage. On the other hand, opposite cases were found where the presence of certain cations decreased the protective effect, for example, towards the corrosion of In4. Additionally, the thermodynamic parameters for adsorption and activation processes were determined; the following formulation properties are considered: the surface tension at cmc (γ_{cmc}), critical micelle concentration (cmc) of the surfactants in aqueous solutions, saturated adsorption amount of the surfactant (Γ_∞) and the minimum average area per surfactant molecule (A_{min}) at the air–water interface. On the bases of the result of small saturated adsorption amount and the large minimum average area per surfactant molecule, it is indicated that the minimum average area of surfactant decreases with the enhanced hydrophilic character of the molecule. A direct relationship has found between the corrosion efficacy (% IE) and Γ_∞. The galvanostatic polarization curves showed that, the inhibitor behaves as mixed type. The observed corrosion data indicate that, the inhibition of carbon steel corrosion is due to the adsorption of the inhibitor molecules on the surface, which follow Langmuir adsorption isotherm. By fitting the obtained experimental data with Langmuir adsorption model, some thermodynamic and kinetic parameters such as adsorption free energy, G_{ads}, equilibrium constant, K_{ads}, were estimated.

Keywords: MIC, Biofilm, Sulfur compounds, Metals, Bisquaternary inhibitor, Galvanostatic polarization.

INTRODUCTION

The corrosion of steel piling structure in marine environment is called low-water corrosion (LWC) indicating that the tidally changing conditions cause MIC [1].

Except of a few cases, COT, fungi, thiobacilli, SRB, manganese reducing- and iron reducing bacteria were regularly detected on LWC-sites. It was generally found that a positive, highly significant correlation exists between cell counts of thiobacilli and those of SRB [2]. Furtheron, an increased amount of corrosion products (mainly iron) at strongly corroded areas were correlated with enhanced contents of sulfur (and sulfate), cell counts, and (microbial and chemical) activities [3-5].

Besides, the quantities of typical metabolites of thiobacilli and SRB like sulfur and sulfate indicate the presence of a sulfuretum. Additionally, iron sulfide and pyrite were detectable at the low-water level. At several sites of strongly corroded areas reduced pH-values and strongly negative redoxpotentials (by reduced oxygen-contents) were measured in the fouling layer. Most probably, these results are due to the metabolic activities of moderately acidophilic organisms (thiobacilli and fungi) or SRB, respectively [6].

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This finding explains why conditions with intermittent oxygenation are so detrimental for metals. Recently it was demonstrated that the compounds CRS (chromium reducable sulfides – pyrite) and sulfate in the surface layer are bioindicators for the strength of corrosion, since their amount was directly correlated with the corrosion rate [8]. As an example for the importance of oxygen, the sulfur cycle on the cited steel sheet pilings in harbours is shown in **Figures 1 & 2** [9].
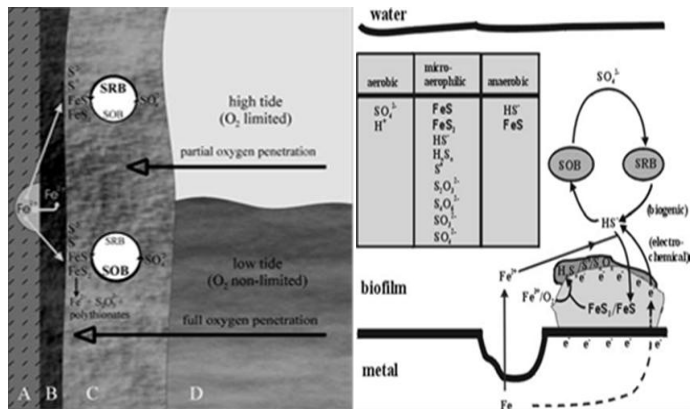

Figure 1 & 2: Importance of oxygen and the sulfur cycle on the cited steel sheet pilings in Harbours

Corrosion inhibition by chemical additives is of great importance in protecting e.g. carbon steel pipe-lines in oil production today. A vast selection of corrosion inhibitors exists, and their performance depends on factors like, size and geometry, affinity for metals (free electron pairs, conjugated bond with electron clouds), length of the alkyl tail, binding strength to the metal substrate, head group atom(s), packing properties, possible polymerization, and ability to react with the corrosion product [10].

In order to understand observations made in such systems, it is beneficial to increase the knowledge about the behavior of the corrosion inhibitor at solid surfaces, liquid interfaces and in bulk phases. The main compound in a corrosion inhibitor formulation is a surface active agent (surfactant), a group of chemicals which has been studied for a wide range of applications in detergency, cosmetics, food etc [11].

This work focuses on the corrosion inhibitor based on heterocyclic bisquats that impedes the corrosion rate when added in small concentrations (ppm). Secondly, the adsorption of In 1 – In 4 surfactants onto the iron surface and their coverage were defined. The investigation was continued to include the inhibition performance against SRB corroded media for these dicationic surfactants which were found to be significantly good.

MATERIALS AND METHODS

Materials

Four heterocyclic amines (1-Dodecylaziridine, 1-Hexadecylaziridine, 1-Hexadecyl-2,5-dihydro-pyrrole, and 1-Hexadecylazepane) and PTC were synthesized following a previously reported work [12]. All studied compounds (*Scheme 1*) were synthesized according to published methods [13]. P-dibromobenzene was obtained from El-Nasr chemicals. All other reagents and solvents were of high purity and used as purchased without any further purification.

Experimental procedure

Heating under phase transfer condition of 1-Dodecylaziridine, 1-Hexadecylaziridine, 1-Hexadecyl-2,5-dihydro-pyrrole, and 1-Hexadecylazepane at 70°C with p-dibromobenzene as alkylating agent in a two-phase system consisting of an organic solvent (chloroform) and 25% aqueous sodium hydroxide solution leads to the formation of the compounds 1,1`-benzene-1,4-diylbis(1-dodecylaziridinium), 1,1`-benzene-1,4-diylbis(1-Hexadecylaziridinium), 1,1`-benzene-1,4-diylbis(1-Hexadecyl-2,5-dihydro-pyrrolium), and 1,1`-benzene-1,4-diylbis(1-Hexadecylazepanium), respectively, in a good yield. All the products were separated and dried [13].

Method of analysis

Elemental analyses were performed using a Varian Elemental and in satisfactory agreement with the calculated values. FT-IR spectra were recorded on a Perkin Elmer- spectrum one spectrophotometer in the 4000-400 cm⁻¹ range using KBr pellets. ¹H NMR spectra were recorded on Varian Gemini 200 MHz (National Research Center, Cairo, Egypt). Surface tension measurements were performed using a Du Nouy Tensiometer (KRUSS K6 Type 4851) with a platinum ring, using the procedure provided by du Nouy.

Electrochemical technique

(Galvanostatic polarization method)

Measurements were performed with the use of a Voltalab 40 PGZ 301 potentiostat. Voltammeograms were recorded at a polarization rate of 10 mV/s. The corrosion rate was monitored in the setup electrochemically and gravimetrically.

Several evaluations were performed when corrosion inhibitors were added into electrolyte such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c, b_a) and corrosion current density (i_{corr}) obtained by extrapolation of the Tafel lines. Aluminum electrodes were cut from the aluminum sheets. The electrodes were of dimensions 1cm x 1cm and were weld from one side to a copper wire used for electric connection. Two methods are in general use for the determination of the corrosion current density (i_{corr}), which is a measure of corrosion rate. These methods are Stern-Geary [14-15] method and intercept [16] method and they are based on anodic and/ or cathodic Tafel curves. Stern-Geary method used for the determination of corrosion current is performed by

extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log (i_{corr}) and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then i_{corr} was used for calculation of inhibition efficiency and surface coverage (θ).

$$\% \ IE = [1 - (i_{corr\,(inh)}/\ i_{corr\,(free)})] \times 100 \qquad (1)$$

$$\theta = [1 - (i_{corr\,(inh)}/\ i_{corr\,(free)})] \qquad (2)$$

where $i_{corr\,(free)}$ and $i_{corr\,(inh)}$ are the corrosion current densities in absence and presence of inhibitors.

Methodology of SRB

**Tube dilution test for determining the minimum inhibitory concentration (MIC) & minimum lethal concentration (MLC):**

> The sample is diluted serially (Bi-fold, 0 – 320 μg / ml) through tubes of liquid nutrient, all tubes are inoculated with an identical sample of a tested microorganism and then incubated then the control containing only the microbe and nutrient [17].

> The turbidity of each successive tube is compared with the control.

> The dilution of the first tube in the series that shows no growth (No turbidity) is the MIC.

> It can be informative to carry this test further by selecting tubes with no visible growth, subculturing them, and retesting this population for susceptibility the lowest sample concentration that completely and permanently suppresses growth in this subset of tubes is called the minimum lethal concentration (MLC).
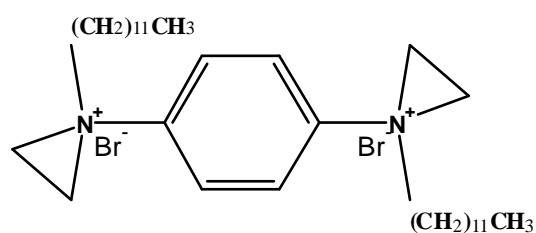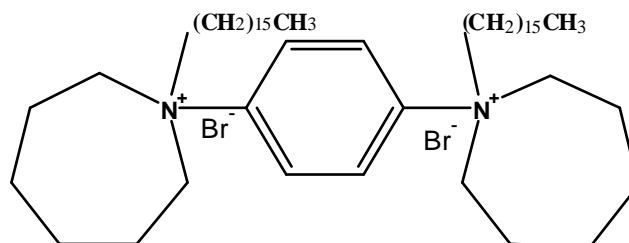

1,1'-benzene-1,4-diylbis(1-dodecylaziridinium)
(In 1)
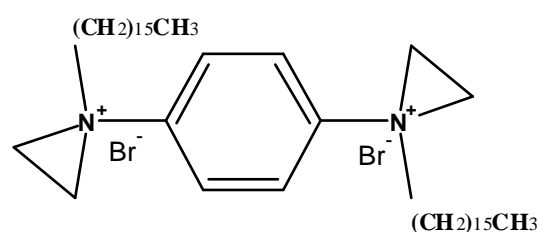
1,1'-benzene-1,4-diylbis(1-hexadecylaziridinium)
(In 2)
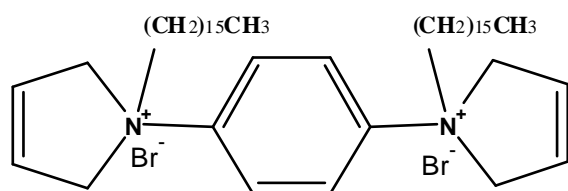
1,1`-benzene-1,4-diylbis(1-hexadecyl-2,5-dihydro-pyrrolium)
(In 4)

1,1`-benzene-1,4-diylbis(1- hexadecylazepanium)
(In 3)

Scheme 1: All bromide compounds

RESULTS AND DISCUSSION

Structural Analyses and Reaction Progress of the Synthesized Inhibitors

The structures of the synthesized aziridinium, pyrrolium and azepanium quaternary ammonium salts have been identified by means of IR, ^{1}H NMR, and elemental analyses (**Tables 1, 2 & 3**). The analytical results that the chemical structures of the cationic surfactants obtained have conformed to the originally designed molecular structures.

For the three reaction systems LLL-PTC, the reaction between the heterocyclic amine and p-dibromobenzene as an alkylating agent progress under phase transfer conditions. The experiments show three kinds of phase appeared when aqueous sodium hydroxide solution and PTC were added. The third liquid phase is formed with different two solvent ($CHCl_3$ and H_2O) and depends both on the aqueous sodium hydroxide concentration as well as $CHCl_3$ addition. These results suggest that substantial quantity of $CHCl_3$ may be dissolved into the organic phase during the reaction until the organic phase depleted whereas the semi-solidification occurred. This is because the $CHCl_3$ moderated the properties of the third phase which could prevent its solidification [18-20].

Table 1: Elemental analyses data for the titled surfactants

Inhibitor	MF	MW	Analysis data calc / found %			
			C	H	N	Br
In 1	$C_{34}H_{62}N_2Br_2$	569	71.7	10.9	4.9	12.5
In 2	$C_{42}H_{78}N_2Br_2$	681	74.0	11.5	4.0	10.4
In 3	$C_{50}H_{94}N_2Br_2$	793	75.7	11.9	3.5	09.0
In 4	$C_{46}H_{82}N_2Br_2$	733	75.3	11.2	3.8	09.7

Table 2: ^{1}H-NMR data (δ, ppm)

Inhibitor	t,-CH$_3$	m,-(CH$_2$)$_n$	m,-CH$_2$-CH$_2$-N+	t,-CH$_2$-N+	CH$_2$(azepane)	CH$_2$(aziridine)	CH$_2$(pyrrolium)	CH=CH(benzene)
In 1	0.96	1.29	1.7	3.03		t, 3.98		S, 8.3
In 2	0.95	1.29	1.8	3.03		t, 3.98		S, 8.3
In 3	0.96	1.30	1.7	3.24	m, 1.2 -m, 1.7- t, 3.24			S, 8.3
In 4	0.97	1.29	1.7	3.24			d, 3.9- m, 5.4	S, 8.3

Table 3: Selected IR frequencies (cm^{-1})

Inhibitor	v (N-tert.)	v(N$^+$-tert.)	v(CH$_2$-stret.)	v(N$^+$- bend.)	v(N- cyclic)	v(CH$_2$-bend.)	v(N-C)	v(Para-)	v(CH=CH)
In 1	3428	3282	2920-2850	1775	1541	1460	1112	1033	1642-548
In 2	3375	3201	2917-2848	1733	1501	1408	1112	1033	1600-543
In 3	3427	3287	2920-2850	1777	1539	1459	1100	1034	1642-551
In 4	3424	3303	2919-2852	1777	1539	1457	1111	1030	1666-556

Surface Tension and Surfactant Parameters

Figure 3 shows the surface tension of the prepared surfactants decreased with increasing concentration of the aqueous solutions, reaching clear break points, which were taken as CMC. **Table 4** lists the **CMC**, the surface tension at the CMC (γ_{cmc}), the maximum surface excess concentration (Γ_∞), and the area occupied per molecule (A_{min}), along with data on the cationic surfactants, it is noted that the surfactants had extremely small CMC; their CMC decreased in the order of In1 > In2 > In3.This suggests that the surfactants easily form aggregates in solution.

That is to say, the gemini surfactants may be adsorbed onto the metal surface through two active groups or atoms, i.e., two nitrogen atoms of heterocyclic ring, thus leading to tight adsorption of gemini molecules on the metal surface and significant corrosion inhibition performance [21].

One might interpret why In3 provides the greatest surface tension as follows: In3 seems to show weak hydrophobicity due to the seven-membered ring, resulting in high surface tension. On the other hand, In2 seems to have poor surface tension due to strong cohesion by the two long hydrocarbon chains. In the case of In1, compact micelles can be formed by strong hydrophobic interactions among the multiple hydrocarbon chains [22].

Table 4: Surface and adsorption parameters of In1 – In4 at 25°

Surface Parameters	In1	In2	In3	In4
γ_{cmc} (mN m^{-1})	29	27	40	------
slope	1.178	0.975	1.354	------
cmc (mol L^{-1})	2 x 10^{-3}	1.6 x 10^{-3}	1 x 10^{-3}	------
A_{min} (nm^2)	8.1	9.8	6.9	------
Γ_∞ (mol m^{-2})	2.06 x 10^{-11}	1.7 x 10^{-11}	2.4 x 10^{-11}	------

Surface excess concentration (Γ_∞) at the air/water interface can be calculated by applying the Gibbs adsorption isotherm equation [23]:

$$\Gamma_{max} = -d\gamma / 2.303RT \ dlog \ C \qquad (1)$$

Where R is the gas constant, T is the absolute temperature, (γ) is the surface tension, and C is the concentration of surfactant.

The cross-sectional molecular area (A_{min}) per molecule can be calculated from the following equation:

$$A_{min} = 10^{18} / N_A\Gamma_\infty \qquad (2)$$

Here N_A is the Avogadro constant.

In regard to the bifunctional surfactants In1−3, there is a slight decrease of Γ_{max}, correlating with the increasing of the hydrophobic methylene chain attached to the heterocyclic ring of the molecules and corresponding to the surface tension reduction. On the other hand, the seven-membered functional surfactant, In3, is still more on the medium side [24].

Table 4 lists the values of A_{min} of In1−3 that were calculated from the linear portion of the plots below the CMC in **Figure 3**. The area per molecule at the air/water interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule. The values of A_{min} of In1 & In2 were 8.1–9.8 nm^2. On the other hand, In3 showed lower area (6.9 nm^2) than inhibitors that with the same heterocyclic ring, In1 & In2, due to the rigid structure with 3-membered ring.
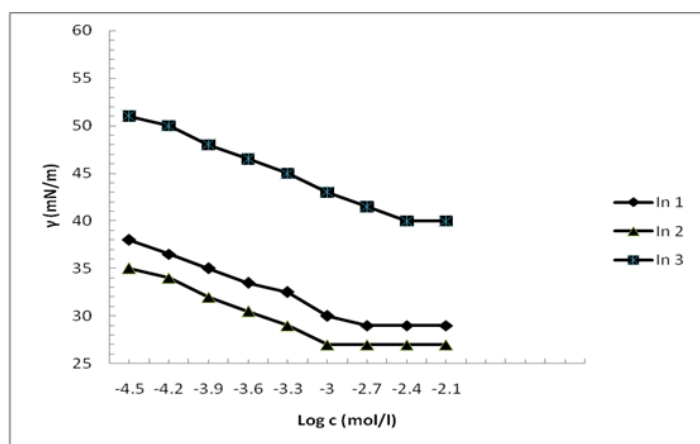

Figure 3: Relationship between logarithm of concentration and surface tension of the prepared inhibitor at 25°C

The surfactant molecules adsorb at the air/water interface by orienting multiple alkyl chains along with skeletal hydrocarbon chains. In addition, the narrow area of In3 owing to the interactions between hydrophobic chains in the surfactant which adsorb at the air/water interface and orient themselves so as to cause high surface activities [25].

The mechanism of corrosion inhibition for the prepared surfactants may be explained on the basis of adsorption behavior and skeletal representation of the proposed mode of adsorption of the investigated surfactant. For such compounds on the basis of the molecular size, the number of active adsorption centers and benzene ring contributes p electrons to the adsorption centers that hence increase the electron density on the adsorption centers [26].

At extremely low concentration of surfactant, the adsorption may take place by horizontal binding to hydrophobic region. This adsorption is favoured by the electrostatic interaction between two quaternary ammonium head groups (N$^+$) and negatively charged metal surface in acid medium. As the surfactant concentration increases, a perpendicular adsorption takes place as a result of two ammonium groups, leads to the gradual formation of multilayers which is already sufficient for significant inhibition. However, this behavior may result in adsorption of In1 & In2 molecules onto the metal surface [27-30].

At higher concentrations of In3, stronger interactions may result in desorption of one or both two ammonium groups from the metal surface.

Biocorrosion Estimation

The problem with MIC is to understand once the biofilm has been formed how metabolic activities of cells induce modifications to be passive layer and how such modifications result in changes to the rates of the corrosion processes [31]. The modifications in the properties of the iron steel/inhibitor layer in natural waters depend strongly on the bacterial population. Therefore, SRB inhibition depletion increased by the electrochemical properties of the passive layer, the corrosion mechanism based on the change of the hydrogenase activity (molecular hydrogen- activating enzyme) which removes hydrogen from the surface of Fe in order to reduce sulfate [32-33]. **Tables 5 & 6** show that SRB population; affect strongly the chemical compositions of the used inhibitors. Results showed a significant increase of the protective effect against SRB in case of In1, In2 & In 3 reached to the optimum. Furthermore, no effect was observed by SRB in the presence of In 4.

Potential Ennoblement

The effect of corrosion inhibitors is always caused by changes in the state of the surface being protected; these changes occur due to adsorption or formation of hardly soluble compounds with metal cations. Corrosion inhibitors reduce the active surface area of a metal and/or change the activation energy of the corrosion process [34].

Table 5: SRB count (CFU/ ml sample)

Conc.	In1	In2	In3	In4
10^{-1}	00.00	00.00	00.00	41
10^{-2}	00.00	00.00	67	230
10^{-3}	374	1.49×10^3	1.23×10^3	3.68×10^3
10^{-4}	4.86×10^3	3.84×10^3	5.56×10^3	6.71×10^3
10^{-5}	6.68×10^3	6.50×10^3	6.69×10^3	6.88×10^3
Control	7.65×10^3	7.65×10^3	7.65×10^3	7.65×10^3

- Sulfur Reducing Bacteria (SRB), *Desulfomonas pigra*, (G⁻).
- CFU: colony forming unit.
- Lethal Concentration (LC).
- Minimum Inhibitory Concentration (MIC).

Table 6: Partial lethal concentration (LC_{50}), minimum inhibition concentration (MIC) and inhibition efficiency (P %) of In1 − In4 against bacterial species

Inhibitor	In1	In2	In3	In4
LC (μg/ml)	10^{-1} , 10^{-2}	10^{-1} , 10^{-2}	10^{-1}	
MIC	0.0038	0.0079	0.018	0.131
P% (10^{-3})	95	80.50	98.40	
P% (10^{-2})	100	100	99	
P% (10^{-1})	100	100	100	

Table 7: Electrochemical corrosion parameters of In1 – In4 in 1M HCl solution (i_o = 1.1025 mA\cm^2)

(ppm)	In1				In2				In3				In4
	i_{corr} mA\cm^2	q	E_i(mV)	% IE	i_{corr} mA\cm^2	q	E_i(mV)	% IE	i_{corr} mA\cm^2	q	E_i(mV)	%IE	
500	0.2006	0.82	-513	82	0.2266	0.79	-516	79.4	0.2880	0.74	-545	74	----
400	0.2803	0.76	-516	74.5	0.3280	0.70	-520	70.0	0.3575	0.68	-550	68	----
300	0.6024	0.45	-518	45	0.4467	0.60	-527	59.5	0.3737	0.66	-552	66	----
200	0.8192	0.26	-521	26	0.5020	0.55	-531	54.5	0.3957	0.64	-553	64	----
100	0.9586	0.13	-547	13	0.6329	0.43	-547	43.0	0.4637	0.58	-555	58	----

The inhibition efficiencies and surface coverage values at different inhibitor concentrations for inhibitor free acid and for each concentration of inhibitor were calculated for the three samples.

Complete inspection of **Table 7** reveals that the corrosion rate of the three samples decreased with the increase of the surfactant concentration. In other words, the corrosion inhibition strengthened with the increase of inhibitor concentration.

It may result from the fact that adsorption amount and the coverage of the surfactant on the electrode surface increases with increasing concentration. Thus, the electrode surface is efficiently separated from the medium.

It is found that the values of **i_{corr}** decrease, while those of inhibition efficiency (**% IE**) increase in the order: In1 >In2 > In3 at of the concentration rang 500-400 ppm. These results confirm the suggestion

that the corrosion resistance of the three samples decreases in the same sequence. On the other hand, at 300-100 ppm of the inhibitor concentration could affect its inhibiting ability in static condition and show less significant protective effect in the order: In3 >In2 > In1 (**Fig. 4**). Considering that the mechanism of the corrosion protection mainly depends on their aggregation ability [35].

It can be found that In1-In3 can act as corrosion inhibitors in 1M HCl, and the inhibition which indicates that the gemini surfactants may be adsorbed onto the steel surface according to Langmuir isotherm.

Surprisingly and interestingly, Langmuir isotherm was found to fit well with the experimental result if the coverage **q** was assumed to be equal to **E%**. According to Langmuir adsorption isothermal equation

$$c/q = 1/K_{ads} + c ,$$

where *c* is the inhibitor concentration and *K* is defined as

$$K_{ads} = 1/55.5 \exp\{G_{ads}/ RT\},$$

Where **C** is the inhibitor concentration, **q** is the fraction of the surface covered, **K**$_{ads}$ is the equilibrium constant of the inhibitor adsorption

process, the value 55.5 is the molar concentration of water in solution in mol/l, **R** is the gas constant, T is absolute temperature and **G**$_{ads}$ is the standard free energy of adsorption process.
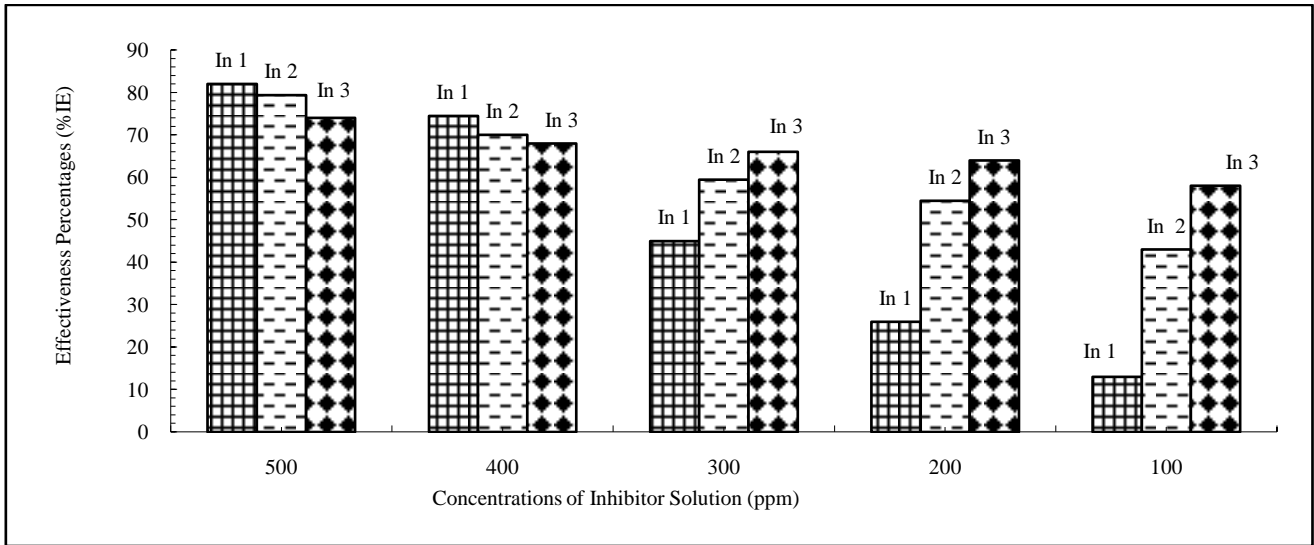

Figure 4: Dependence of the corrosion rate effectiveness of carbon steel in water containing HCl (1M) + prepared inhibitor on the concentration of 500-100 ppm

Figs. 5-7 show the dependence of the fraction of the surface covered **C/q** as a function of the concentration (**C**) of the synthesized inhibitors.
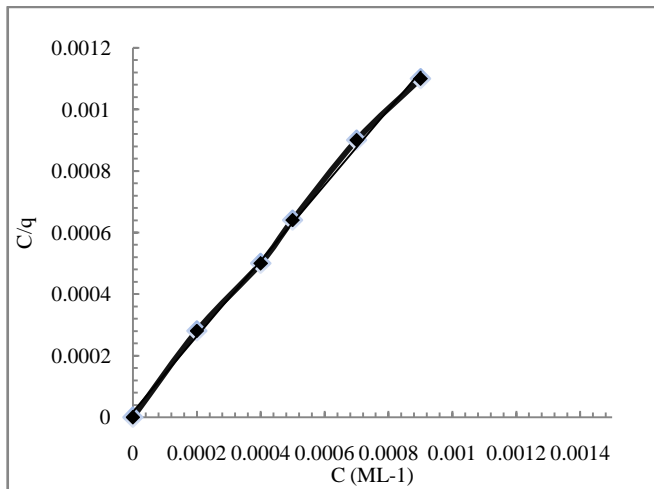

Figure 5: Langmiur adsorption isotherm (Ci/q vs. Ci) of In 1 on carbon steel surface in 1M HCl solution

The slope of the isotherm deviates from unity for all desired inhibitor. This deviation may be explained on the basis of interaction between the adsorbed species on the metal surface by mutual repulsion or attraction [36, 37], i.e., the inhibitor acts effectively at the metal solution/interface.

The obtained plots of the inhibitors are linear and the intercept permits the calculation of the equilibrium constant **K**$_{ads}$ which are 2×10^5, 4×10^5 and 2×10^5 M^{-1} for In 1, In 2 & In 3, respectively. The relatively high value of the adsorption equilibrium constant reflects the high adsorption ability of this compound on the metal surface [38].

The values of **K**$_{ads}$ which indicate the binding power of the inhibitors to the carbon steel surface leads to calculation of the adsorption energy.
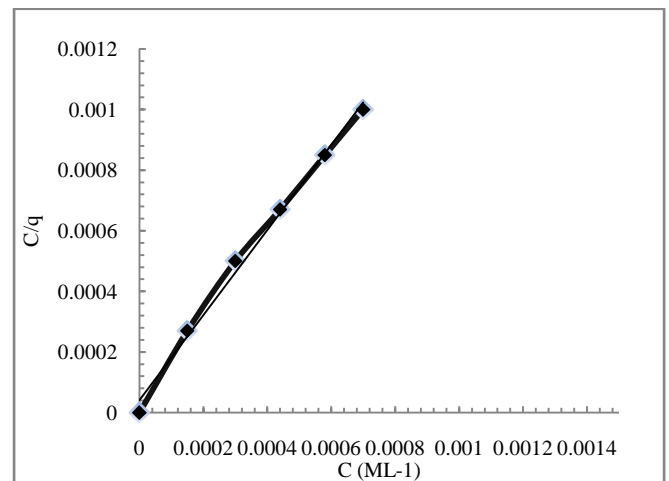

Figure 6: Langmiur adsorption isotherm (Ci/q vs. Ci) of In 2 on carbon steel surface in 1M HCl solution
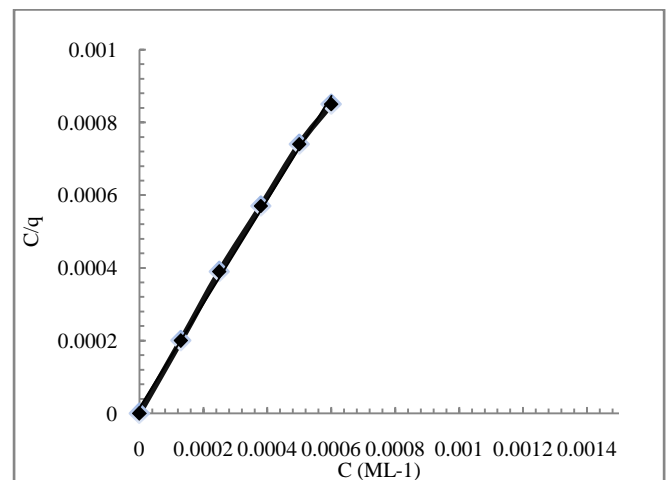

Figure 7: Langmiur adsorption isotherm (Ci/q vs. Ci) of In 3 on carbon steel surface in 1M HCl solution

Values of $\mathbf{G_{ads}}$ are -36.8, -35 and -36.8 kJ mol^{-1} for In 1, In 2 & In 3, respectively.

The negative value of $\mathbf{G_{ads}}$ means that the adsorption of the prepared inhibitors carbon steel surface is a spontaneous process and also show a strong interaction of the inhibitor molecule onto the carbon steel surface [39, 40].

Generally, values of $\mathbf{G_{ads}}$ around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). While those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [41,42].

The calculated $\mathbf{G_{ads}}$ values indicated that the adsorption mechanism of the prepared inhibitors on carbon steel in 1 M HCl solution is a mixed from physical and chemical adsorption [43, 44].

CONCLUSIONS

- ➢ Cation-active corrosion inhibitors hinder the cathodic reactions or the active dissolution of the metal for the corrosion of carbon steel surface in hydrochloric acid solution.
- ➢ The effect of corrosion inhibitors is always caused by changes in the state of the surface being protected; these changes occur due to adsorption or formation of hardly soluble compounds with metal cations. Surfactant compounds adsorb on carbon steel surface according to the Langmuir adsorption isotherm.
- ➢ The inhibitors increase the value of activation energy of corrosion and consequently, decrease the rate of dissolution of carbon steel in HCl solution.
- ➢ The galvanostatic polarization data indicate that the inhibition efficiency increased with increasing concentration of the inhibitor, ($\mathbf{\eta\%}$) reached to 82% at 500 ppm of the inhibitor.
- ➢ Corrosion inhibitors reduce the active surface area of a metal and/or change the activation energy of the corrosion process. Corrosion inhibitors can also passivate a metal if they form hardly soluble salts or complexes with its ions. If strong bonds between ammonium cations and the metal are formed, passivation may be provided by the adsorption of the inhibitor.
- ➢ The investigated inhibitors were suggested to be mixed from physical and chemical adsorption on the steel electrode on the basis of the high values of the adsorption desorption equilibrium constant, $\mathbf{K_{ads}}$, and the free energy of adsorption, $\mathbf{G_{ads}}$.

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