

# Phase Transfer Synthesis of Novel Based Surfactants: Role of Biocorrosion Inhibition

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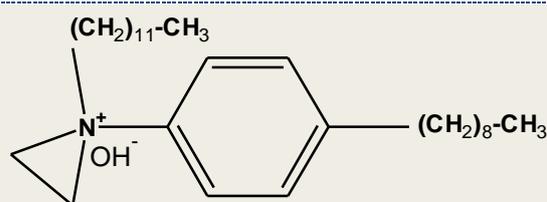
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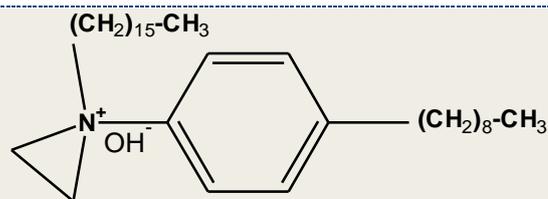
## ABSTRACT

Two types of corroded medium, acid and SRB, could be evaluate novel aziridinium, pyrrolium and azepanium quaternary ammonium salts as corrosion inhibitors at the concentration range of 500 - 100 ppm in 1M HCl. Quaternization of a series of heterocyclic amines with 4-nonyl phenol in the presence of aqueous sodium hydroxide under phase transfer conditions in chloroform as a solvent was performed (Scheme 1). Active ingredients of those inhibitors included long chain hydrocarbon heterocyclic amines were confirmed using FTIR, <sup>1</sup>H NMR, and elemental analyses. The results, which include the corrosion and electrochemical testing data, showed that tested corrosion inhibitors In1 - In4 are effective in studied range of concentration and the corrosion effectiveness of tested quats increases toward In1- In3 with increase the number of member rings. 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. Apparently, the polar group makes it possible to lengthen the hydrophobic fragment of the inhibitor without significantly disturbing its hydrophilic-lipophilic balance and thus make the inhibitor not only more hydrophobic but also more soluble in water, which enhances its technological properties. For evaluation of SRB inhibition efficacy, microbial activity was monitored and cell counts were determined. All inhibitors were able to reduce microbial activity. The growth of the reference SRB (*Desulfomonas pigra*) was shown to be completely inhibited by In1- In3. In contrast, In4 had only a slight effect as being due to the presence of pyrrolium cation which may also be achieved due to decreasing the protective effect process. In this work, the thermodynamic parameters for adsorption and activation processes were determined; the following formulation properties are considered: the surface tension at cmc ( $\gamma_{cmc}$ ), critical micelle concentration (cmc) of the surfactants in aqueous solutions, saturated adsorption amount of the surfactant ( $\Gamma_{\infty}$ ) 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  $\Gamma_{\infty}$ .

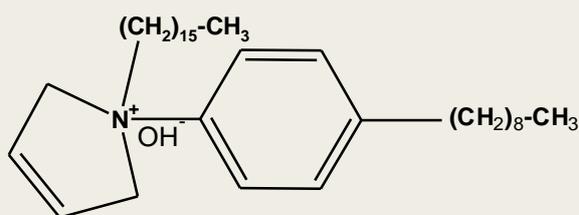
## Scheme 1



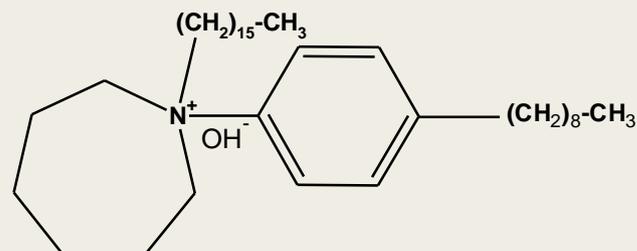
**1-dodecyl-1-(4-nonylphenyl)aziridinium  
(In1)**



**1-hexadodecyl-1-(4-nonylphenyl)aziridinium  
(In2)**



**(In4)  
1-hexadodecyl-1-(4-nonylphenyl)-2,5-dihydro-pyrrolium  
nonylphenyl)azepanium**



**(In3)  
1-hexadodecyl-1-(4-**

**Keywords:** MIC, Biofilm, Sulfur compounds, Metals, Ennoblement, Galvanostatic polarization.

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## 1. INTRODUCTION

The biocorrosion of metals is a serious economic problem. The economic value of biocorrosion must amount on a worldwide scale to several billions of Euro annually (Beech and Tapper, 1999). If by improved diagnosis, materials selection, modification of environmental conditions, etc a part of this sum could be saved, a considerable amount of money would become available for other, more useful purposes (Gehrke *et al.*, 1998). Two types of corrosion need to be distinguished: localized and flat-spread corrosion (Von Re`Ge and Sand, 1999).

Localized corrosion develops preferentially under aeration or concentration elements. This may result from a microcolony under which, due to its oxygen consumption by metabolism anaerobic zones develop, whereas the adjacent surface without microcolony remains aerobic. Consequently, under the microcolony an anode is formed and the adjacent area becomes cathodic. Dissolution of the metal may result. Also iron(III) hydroxide precipitates (tubercles) often cause localized corrosion, although the tubercles may be only an indication of the corrosion process, not the reason.

Flat-spread corrosion phenomena have often been found to be associated with SRB under biofilms and/or the presence of acid-forming microorganisms. SRB promote corrosion by the formation of their endproduct sulfide, which reacts with the anodically produced iron(II) ions to nearly insoluble iron sulfide. The latter acts, if in contact with the metal, as an enlargement of the cathode, thus enhanced the corrosion. Especially in connection with metal biocorrosion bacteria of the sulphur, nitrogen, iron, and manganese cycles play an important role. The typical metabolism products corresponding with the growth of such microorganisms as sulphur, reduced sulphur compounds (thiosulphate, sulfide, polythionate) and nitric oxide as well as iron(III) and manganese-IV-ions show in

general strong corrosive properties since they support the cathodic subprocess of the metal dissolution directly due to their high oxidation potential (Sand and Gehrke, 2004).

On the other term, the adsorption is the formation of a layer of gas, liquid or solid on the surface of a solid or liquid (Landaus *et al.*, 2008). A distinction is made between chemisorption, where the attachment is caused by chemical bonds, and physisorption, where the adsorption is due to attractive forces like van der Waals forces. The two main forces resulting in physisorption type of adsorption are:

**Hydrophobic force:** The strong interaction between water molecules results in a repulsion of the alkyl chain from the aqueous phase. This force will always be present and favor the adsorption. **Electrostatic forces:** A negatively charged surface will attract cationic surfactants and repel anionic surfactants while a positively charged surface will do the opposite. The adsorption process can be investigated by methods like depletion method, ellipsometry, surface plasmon resonance and quartz crystal microbalance. In the depletion method (Chamritski *et al.*, 2004) the surface excess is determined by measuring the depletion of surfactant in the aqueous solution after adsorption to a surface of large area. This method requires a known surface area, and yield equilibrium values of the surface excess.

The chemistry of corrosion inhibitors surfactants was visualized. The structures were found to be similar to the bulk aggregates (Féron and Roy, 2000). For special cases it is possible to have a bilayer adsorbate, namely if the packing of the molecules is analogous to that of the lyotropic liquid crystalline phases with a lamellar structure (Marconnet *et al.*, 2005). The classification of corrosion inhibitors into cathodic, anodic and mixed ones implies that there is a relationship between the protection mechanism and the changes in electrochemical kinetics caused by these compounds (De La Rosa and Yu, 2005). In most cases, passivating inhibitors suppress the anodic dissolution of metals, but passivation may also be achieved due to acceleration of the cathodic reaction by an inhibitor, as is the case in passivation of iron with dinitrobenzoate anion (Salvago and Magagnin, 2001). Corrosion inhibitors can also passivate a metal if they form hardly soluble salts or complexes with its ions. If strong bonds between higher carboxylate anions and the metal are formed, passivation may be provided by the adsorption of the inhibitor, as was first observed in sodium N-phenylanthranilate (SPA) solutions (Yang and McCrery, 2000).

The adsorption process of a model corrosion inhibitor, alkyltrimethylammonium bromide, onto iron and cementite surfaces has been investigated by Riggs, O.L. It has also been demonstrated how the surface aggregate structure could be manipulated to be film-forming by addition of a surfactant (Riggs *et al.*, 2001). In contrast, study of the protective effects of 100 ppm aliphatic tertiary diamines approached 66 to 89 % protective values by Murav'eva *et al.* (2003).

## 2. EXPERIMENTAL

### 2.1. Materials

Heterocyclic amines (1-Dodecylaziridine, 1-Hexadecylaziridine, 1-Hexadecyl-2,5-dihydro-pyrrole, and 1-Hexadecylazepane) and PTC were synthesized following a previously reported work (Hanan, 2008). All studied compounds (Scheme 1) were synthesized according to published methods (Hanan, 2007). 4-Nonyl phenol was obtained from El-Nasr chemicals. All other reagents and solvents were of high purity and used as purchased without any further purification.

### 2.2. Synthesis Procedure

Heating under phase transfer condition of 1-Dodecylaziridine, 1-Hexadecylaziridine, 1-Hexadecyl-2,5-dihydro-pyrrole, and 1-Hexadecylazepane at 70°C with 4-Nonyl phenol as alkylating agent in a three-phase system

consisting of an organic solvent (chloroform) and 15% aqueous sodium hydroxide solution leads to the formation of the compounds 1-Dodecyl-1-(4-nonylphenyl)aziridinium, 1-Hexadodecyl-1-(4-nonylphenyl)aziridinium, 1-Hexadodecyl-1-(4-nonylphenyl)-2,5-dihydro-pyrrolium, and 1-Hexadodecyl-1-(4-nonylphenyl)azepanium, respectively, in good yields. All the products were separated and dried (Hanan, 2007).

### 2.3. 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  $\text{cm}^{-1}$  range using KBr pellets.  $^1\text{H}$  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.

### 2.4. 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  $\mu\text{g}$  / 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 (Campbell *et al.*, 2004).
- 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).

## 3. ELECTROCHEMICAL TECHNIQUE

### 3.1. Galvanostatic Polarization Method

Measurements were performed with the use of a Voltalab 40 PGZ 301 potentiostat. Voltammograms 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 ( $E_{\text{corr}}$ ), cathodic and anodic Tafel slopes ( $b_c$ ,  $b_a$ ) and corrosion current density ( $i_{\text{corr}}$ ) 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 ( $i_{\text{corr}}$ ), which is a measure of corrosion rate.

These methods are Stern-Geary (Washizu *et al.*, 2001) method and intercept (Olsen *et al.*, 2000; Linhardt, 2006) 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  $\log(i_{\text{corr}})$  and the corresponding corrosion potential ( $E_{\text{corr}}$ ) for inhibitor free acid and for each concentration of inhibitor. Then  $i_{\text{corr}}$  was used for calculation of inhibition efficiency and surface coverage ( $\theta$ ).

$$\% \text{IE} = \left[ 1 - \left( \frac{i_{\text{corr}}(\text{inh})}{i_{\text{corr}}(\text{free})} \right) \right] \times 100 \quad (1)$$

$$q = [1 - (i_{\text{corr (inh)}} / i_{\text{corr (free)}})] \quad (2)$$

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

## 4. RESULTS AND DISCUSSION

### 4.1. Structural Analyses and Reaction Progress of the Synthesized Inhibitors

The structures of the synthesized aziridinium, pyrrolidinium and azepanium quaternary ammonium salts have been identified by means of IR,  $^1\text{H}$  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 nonyl phenol 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 ( $\text{CHCl}_3$  and  $\text{H}_2\text{O}$ ) and depends both on the aqueous sodium hydroxide concentration as well as  $\text{CHCl}_3$  addition. These results suggest that substantial quantity of  $\text{CHCl}_3$  may be dissolved into the organic phase during the reaction until the organic phase depleted whereas the semi-solidification occurred. This is because the  $\text{CHCl}_3$  moderated the properties of the third phase which could prevent its solidification (Maw-Ling and Yao-Hsuan, 2003; Kazem and Mirzaagha, 2005; Sharma *et al.*, 2005). Treatment of nonyl phenol with chloroform (trichloromethane) in the presence of hydroxide ion results in the synthesis of dichlorocarbene:  $\text{CCl}_2$ , and the phenoxide ion that is sufficiently nucleophilic to be attacked by amines.

The inhibition performance of the polycation-surfactant complex was found to be significantly better than a comparable film-forming system.

Table-1. Elemental analyses data for the titled surfactants.

Inhibitor	MF	MW	Analysis data calc / found %			
			C	H	N	O
In 1	$\text{C}_{29}\text{H}_{53}\text{NO}$	431	80.0	12.3	3.2	3.7
In 2	$\text{C}_{33}\text{H}_{61}\text{NO}$	487	81.3	12.5	2.9	3.3
In 3	$\text{C}_{37}\text{H}_{69}\text{NO}$	543	81.9	12.7	2.6	2.9
In 4	$\text{C}_{35}\text{H}_{63}\text{NO}$	513	81.9	12.3	2.7	3.0

Table-2.  $^1\text{H}$ -NMR data ( $\delta$ , ppm).

Inhibitor	t, $\text{CH}_2$	m, $-\text{CH}_2-\text{CH}_2-$	m, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	m, $(\text{CH}_2)_n$	m, $\text{CH}_2-\text{CH}_2-\text{N}^+$	t, $-\text{CH}_2-\text{N}^+$	$\text{CH}_2$ (azepanium)	$\text{CH}_2$ (aziridinium)	$\text{CH}_2$ (pyrrolidinium)	$\text{CH}=\text{CH}$ (benzene)
In 1	0.98	2.6	1.62	1.28	1.7	3.3		t, 3.98		m, 7.6-8
In 2	0.95	2.6	1.62	1.28	1.8	3.3		t, 3.98		m, 7.6-8
In 3	0.96	2.6	1.62	1.3	1.7	3.24	m, 1.3 - m, 1.7- t, 3.24			m, 7.6-8
In 4	0.97	2.6	1.62	1.28	1.7	3.5			d, 3.9- m, 5.4	m, 7.6-8

Table-3. Selected IR frequencies (cm<sup>-1</sup>).

Inhibitor	v (N-tert.)	v(N <sup>+</sup> -tert.)	v(CH <sub>2</sub> -stret.)	v(N <sup>+</sup> -bend.)	v(N-cyclic)	v(CH <sub>2</sub> -bend.)	v(N-C)	v(Para-)	v(CH=CH)
In 1	3400	3252	2929,2853	1798	1549	1458	1119	1034	1641-553
In 2	3438	3062	2921-2854	1774	1541	1459	1118	1058	1662-556
In 3	3412	3047	2923-2850	1798-1839	1541	1450	1113	1032	1667-547
In 4	3435	3049	2939-2856	1784	1546	1451	1116	1030	1666-540

#### 4.2. Surface Tension and Surfactant Parameters

The surface tension isotherms of solutions of the new surfactant compounds (In1 – In3), given in Figure 1, show characteristic shapes. The surface tension isotherms were used to determine surfactant parameters of the new compounds: CMC, surface tension at CMC ( $\gamma_{cmc}$ ), and maximum surface excess ( $\Gamma_{max}$ ). The data of these parameters are summarized in Table 4 which revealed that inhibitors 2, and 3, begin with a much decrease of surface tension at very low concentrations, compared to inhibitor 1. The minimum levels of surface tension caused by addition of the synthesized inhibitors are lowest for In 2 (28 mN m<sup>-1</sup>), while being 31 and 35 mN m<sup>-1</sup> for inhibitors 1 & 3, respectively. Prior to inhibitors 1, 2, and 3, the slopes of surface tension reduction change to horizontal and ranging from 1.166 to 1.947.

The CMC for compounds 1–3, derivable from high concentration points of inversion of the respective surface tension isotherms (Figure 1), range from a minimum value of 1.3 x 10<sup>-3</sup> mol L<sup>-1</sup> for compound 3 to a maximum value of 2.4 x 10<sup>-3</sup> mol L<sup>-1</sup> for compound 1.

Values of the maximum surface excess ( $\Gamma_{max}$ ) of the saturated interface were calculated in a typical way from the linear part of the surface tension isotherm, according to Gibbs's equation in the form (Tebo *et al.*, 2004; Washizu *et al.*, 2004; Elewady *et al.*, 2008):

$$\Gamma_{max} = -d\gamma / 2.303RT \, d \log C \quad (1)$$

where  $\gamma$  = surface tension, C = concentration of the surfactant below CMC, T = absolute temperature, and R = gas constant.

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

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

Here  $N_A$  is the Avogadro constant.

This shows again that constructing relations between  $\Gamma_{max}$  and the structure of a surfactant molecule is a problem since other parameters such as solubility in the bulk phase or intermolecular interactions also correlating with the dimensions and geometry of the surfactant molecules have to be taken into consideration. Actually, these data are clearly aligned with the structural features of the new surfactants. Here, the micellization process is dominated by the hydrophobic content of the surfactant molecule.

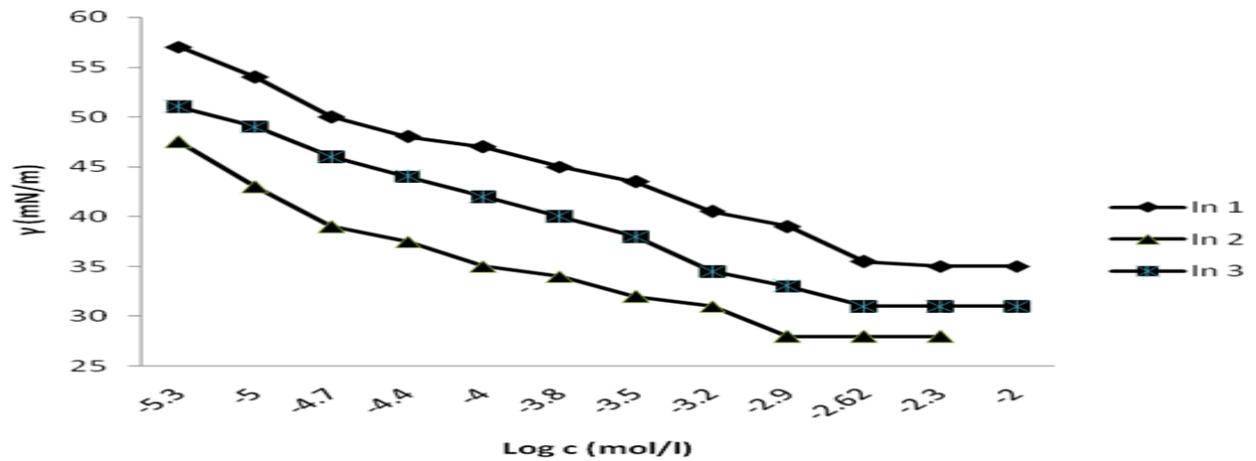


Figure-1. Relationship between logarithm of concentration and surface tension of the prepared inhibitor at 25°C.

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

Surface Parameters	In1	In2	In3	In4
$\gamma_{cmc}$ (mN m <sup>-1</sup> )	35	28	31	-----
slope	1.242	1.166	1.947	-----
cmc (mol L <sup>-1</sup> )	$2.4 \times 10^{-3}$	$2 \times 10^{-3}$	$1.3 \times 10^{-3}$	-----
$A_{min}$ (nm <sup>2</sup> )	7.65	8.30	4.90	-----
$\Gamma_{\infty}$ (mol m <sup>-2</sup> )	$2.18 \times 10^{-11}$	$2 \times 10^{-11}$	$3.4 \times 10^{-11}$	-----

#### 4.3. Surfactant Adsorption

Of prime importance is the fact that the adsorption of monomers is electrostatically driven, different techniques have shown that In 1-3 were adsorbed with the head-group towards the surface while the hydrocarbon tail protrudes into the solution (Laurier, 2000). The adsorption of surfactant continues with the hydrophilic group protruding into the solution and the hydrocarbon tail mingling with the adsorbed monomers, driven by the hydrophobic force, until the surface is saturated.

Surfactants will form surface aggregates for the same reason they form aggregates in the bulk solution. The system gain energy in reducing the contact area between the carbon chains and the aqueous surroundings. This energy gain is the driving force for the process. The structure of the aggregate is partly determined by the molecular packing parameter.

Further increases in surfactant concentrations result in other types of aggregates such as lamellar structures and rode-like micelles that can form in solution as well as analogous bilayers and/or multilayers that form at interfaces (Müller *et al.*, 2001; Tomokazu *et al.*, 2004). Surfactants with highly charged head groups (In 3) form spherical micelles in the bulk solution. When adsorbed onto surfaces with which the interaction is small, the surface aggregates will be oblate spheres. However, if the interaction with the surface is strong this may influence the geometry (Sizaya and Andrushko, 2004).

#### 4.4. 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 (Busalmen *et al.*, 2002; Lai and Bergel, 2002). 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 (Lai and Bergel, 2002; Tebo et al., 2005).

Tables 5 & 6 showed 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.

Table-5. SRB count (CFU/ ml sample)

Conc.	In1	In2	In3	In4
10 <sup>-1</sup>	00.00	00.00	00.00	231
10 <sup>-2</sup>	00.00	00.00	00.00	1.25x10 <sup>3</sup>
10 <sup>-3</sup>	00.00	2.15x10 <sup>3</sup>	128	4.31x10 <sup>3</sup>
10 <sup>-4</sup>	5.21x10 <sup>3</sup>	4.45x10 <sup>3</sup>	4.63x10 <sup>3</sup>	6.28x10 <sup>3</sup>
10 <sup>-5</sup>	6.98x10 <sup>3</sup>	6.67x10 <sup>3</sup>	5.98x10 <sup>3</sup>	7.09x10 <sup>3</sup>
Control	7.65x10 <sup>3</sup>	7.65x10 <sup>3</sup>	7.65x10 <sup>3</sup>	7.65x10 <sup>3</sup>

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

Table-6. Partial Lethal Concentration (IC<sub>50</sub>), Minimum Inhibition Concentration (MIC) and Inhibition Efficiency (P%) of In1 – In4

Inhibitor	In1	In2	In3	In4
LC (µg/ml)	10 <sup>-1</sup> , 10 <sup>-2</sup> , 10 <sup>-3</sup>	10 <sup>-1</sup> , 10 <sup>-2</sup>	10 <sup>-1</sup> , 10 <sup>-2</sup>	
MIC	0.00087	0.0084	0.0024	0.1720
P% (10 <sup>-4</sup> )	32.00	41.80	39.50	
P% (10 <sup>-3</sup> )	100	72	98	
P% (10 <sup>-2</sup> )	100	100	100	

#### 4.5. Potential Ennoblement

Table-7. Electrochemical corrosion parameters of In1 – In4 in 1M HCl solution (i<sub>0</sub> = 1.1025 mA\cm<sup>2</sup>)

In. Conc. (ppm)	In1				In2				In3				In4
	i <sub>corr</sub> mA\cm <sup>2</sup>	q	E <sub>i</sub> (mV)	% IE	i <sub>corr</sub> mA\cm <sup>2</sup>	q	E <sub>i</sub> (mV)	% IE	i <sub>corr</sub> mA\cm <sup>2</sup>	q	E <sub>i</sub> (mV)	% IE	
500	0.0975	0.91	-588.8	91.2	0.1219	0.90	-559.9	90.0	0.0807	0.93	-509	92.7	
400	0.1155	0.90	-596.1	89.5	0.1285	0.88	-568.4	88.3	0.1786	0.84	-521.9	84.4	
300	0.1899	0.83	-602	82.8	0.1306	0.88	-572.4	88.2	0.1786	0.84	-550.9	83.8	
200	0.1977	0.82	-604	82.0	0.1325	0.88	-575.6	88.0	0.2216	0.80	-564.3	80.0	
100	0.1993	0.82	-612	81.9	0.1910	0.83	-579.8	83.0	0.2508	0.77	-570.6	77.0	

On the basis of the rate of potential mainly affected and increased by biological and physicochemical factors, the corrosion of iron steel has investigated by the presence of new four inhibitors, In 1-4. The free corrosion potential (E<sub>corr</sub>) is the first indicator used to characterize the influence of the prepared inhibitors on the electrochemical behavior of iron steel. During a 30-minute immersion period in 1M HCl, potential ennoblement progressed until the E<sub>corr</sub> reached high values in the presence of In 1-3 (Table 7). In the case of In 4, the chemical composition and

the microstructure of iron steel have no influence on the tendency of the metal to enoble as long as it is able to form a passive layer due to the poor solubility of such compounds in water. From the results shown in Table 7, it is clear that at the same inhibitor concentration, the effectiveness of the selected surfactants as corrosion inhibitors (% IE) is increased by increasing both the number of methylene units (at low concentration) and the number of member rings (at high concentration). Consequently, in the context of corrosion inhibition using surfactants, the critical micelle concentration marks an effective boundary condition below which surfactant adsorption is typical below the monolayer level, and above which adsorption can consist of multiple layers of surfactant (Miyata *et al.*, 2004).

Contrary to previous observations, the  $E_{\text{corr}}$  ennoblement doesn't play a direct role. This study was discussed experimentally by monitoring  $E_{\text{corr}}$  at five different concentrations: 100-500 ppm (Figure 2). The results at the range 100-300 ppm, there is a significant inhibition with increasing methylene unit rather than the number of member rings. Similarly to the findings inhibition of In 2 compared to In1 and In3 at the concentration range 100-300 ppm was shown. At these concentrations, as the surfactant molecules increases, the tendency for physical adsorption and aggregation increases, and the associated aggregation or adsorption is evidenced by decreasing surface tension. Further increases in surfactant concentration (at 500 ppm) of In 3 lead to a gradual increase in the following order  $3 > 1 > 2$ . This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration. The dependence of the protective effects of the amines on their concentrations necessitates prompt supply of an inhibitor to the protected surface.

In Figure 2 the corrosion density ( $i_{\text{corr}}$ ) of the sample after corrosion process in the presence of In 1-3 are presented. Figure 2 shows that corrosion rates were almost equal at low concentration of the inhibitor. On the other hand, the concentration at which the inhibitor could affect its inhibiting ability in static condition and show the best protective effect is 500 ppm. Considering that the mechanism of the corrosion protection mainly depends on their aggregation ability (Tani *et al.*, 2003; Hegazy, 2009).

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:

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

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

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

where  $C$  is the inhibitor concentration,  $q$  is the fraction of the surface covered,  $K_{\text{ads}}$  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  $G_{\text{ads}}$  is the standard free energy of adsorption process.

Figures 3-5 show the dependence of the fraction of the surface covered  $C/q$  as a function of the concentration ( $C$ ) of the synthesized inhibitors. 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 (Ugryumov *et al.*, 2005; Boris *et al.*, 2009) 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  $K_{\text{ads}}$  which are  $0.33 \times 10^7$ ,  $10^5$  and  $10^5 \text{ M}^{-1}$  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 (Sabine *et al.*, 2007). The values of  $K_{\text{ads}}$  which indicate the binding power of the inhibitors to the carbon steel surface leads to calculation of the adsorption energy. Values of  $G_{\text{ads}}$  are  $-35.8$ ,  $-38.5$  and  $-38.5 \text{ kJ mol}^{-1}$  for In 1, In 2 & In 3, respectively.

The negative value of  $G_{ads}$  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 (Lai and Bergel, 2000; Busalmen *et al.*, 2002). Generally, values of  $G_{ads}$  around  $-20 \text{ kJ mol}^{-1}$  or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). While those more negative than  $-40 \text{ kJ mol}^{-1}$  involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (Kuznetsov, 2002). The calculated  $G_{ads}$  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 (German, 2010).

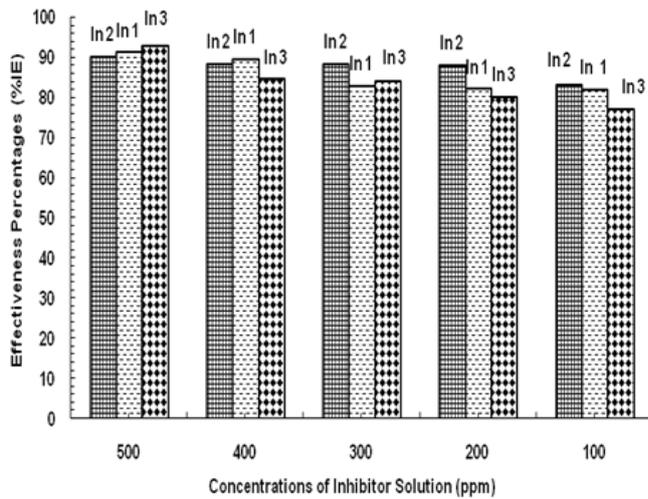


Figure-2. Dependence of the corrosion rate effectiveness of carbon steel in water containing 1M HCl + prepared inhibitor on the concentration of 500-100 ppm

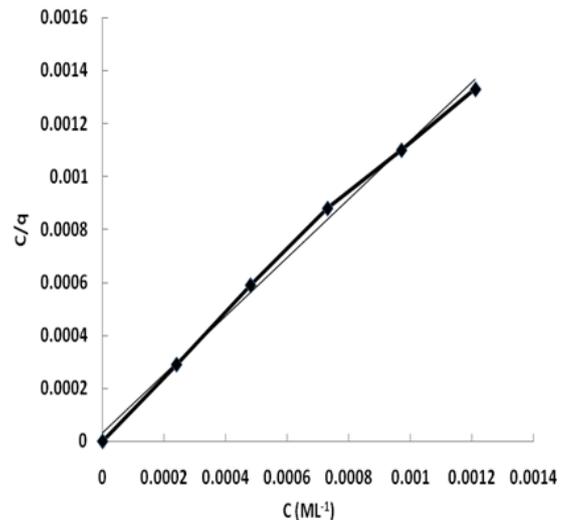


Figure-3. Langmuir adsorption isotherm ( $C_i/q$  vs.  $C_i$ ) of In 1 on carbon steel surface in 1M HCl solution.

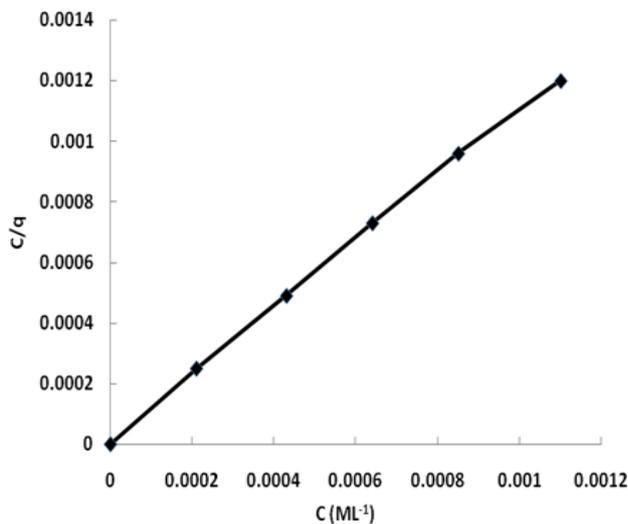


Figure-4. Langmuir adsorption isotherm ( $C_i/q$  vs.  $C_i$ ) of In 2 vs.  $C_i$  of on carbon steel surface in 1M HCl solution.

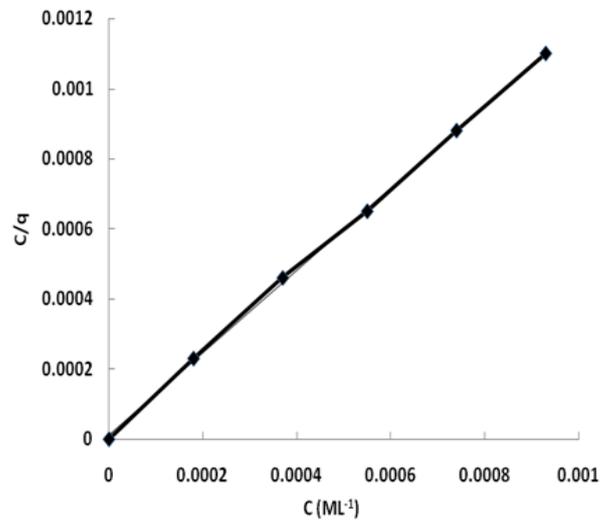


Figure-5. Langmuir adsorption isotherm ( $C_i/q$  vs.  $C_i$ ) of In 3 on carbon steel surface in 1M HCl solution.

### 5. CONCLUSIONS

- The investigated surfactant compounds act as inhibitors for the corrosion of carbon steel surface.
- 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.
- Polarization data showed that these investigated surfactant compounds served as effective corrosion inhibitors by blocking the active sites of the metal surface.
- The galvanostatic polarization data indicate that the inhibition efficiency increased with increasing concentration of the inhibitor, ( $\eta\%$ ) reached to 92.7%.
- 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,  $K_{ads}$ , and the free energy of adsorption,  $G_{ads}$ .

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