

## Efficient Complex Surfactants from the Type of Fatty Acids as Corrosion Inhibitors for Mild Steel C1018 in CO<sub>2</sub>-Environments

Vagif M. Abbasov<sup>†</sup>, Hany M. Abd El-Lateef<sup>‡,§,\*</sup>, Leylufer I. Aliyeva<sup>†</sup>, Ismayil T. Ismayilov<sup>†</sup>,  
Elmar E. Qasimov<sup>†</sup>, and Mamedova M. Narmin<sup>†</sup>

<sup>†</sup>Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, AZ1025 Baku, Azerbaijan

<sup>‡</sup>Chemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt.

\*E-mail: [Hany\\_shubra@yahoo.co.uk](mailto:Hany_shubra@yahoo.co.uk)

(Received June 24, 2012; Accepted November 23, 2012)

**ABSTRACT.** The efficiency of three complex surfactants based on sunflower oil and nitrogen containing compounds as corrosion inhibitors for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution, has been determined by weight loss and LPR corrosion rate measurements. These compounds inhibit corrosion even at very low concentrations. The inhibition process was attributed to the formation of an adsorbed film on the metal surface that protects the metal against corrosive media. The inhibition efficiency increases with increasing the concentration of the studied inhibitors. Maximum inhibition efficiency of the surfactants is observed at concentrations around its critical micellar concentration (CMC). Adsorption of complex surfactants on the mild steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Energy dispersive X-ray fluorescence microscopy (EDRF) observations of the electrode surface confirmed the existence of such an adsorbed film.

**Key words:** Complex surfactants, Corrosion, Sunflower oil, Mild steel, Adsorption isotherm

### INTRODUCTION

Corrosion is a fundamental process playing an important role in economy and safety, particularly for metals and alloys.<sup>1</sup> Various type of steels including stainless-steel is a major construction material and is extensively used throughout industry (chemical and electrochemical industries, medical, nuclear, petroleum, power, and food production), and also in everyday life. However, it suffers from a certain type of corrosion within some environments. It is for this reason that the electrochemical properties of steel are the subject of many studies.<sup>2–10</sup>

Carbon dioxide (CO<sub>2</sub>) corrosion is one of the major problems in oil and gas industry, costing billions of dollars every year.<sup>11</sup> In CO<sub>2</sub> corrosion, CO<sub>2</sub> dissolves and hydrates to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which then dissociates into bicarbonate, carbonate and hydrogen ions.<sup>12–20</sup> The use of inhibitors is one of the most practical methods for protection against corrosion. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevent transportation of water and corrosion-active species on the metal surface. Thus, there is always a need to develop new corrosion inhibitors.

Inhibitors which reduce corrosion on metallic materials

can be divided into four kinds: (i) inorganic inhibitors, (ii) organic inhibitors, (iii) surfactant inhibitors, and (iv) mixed material inhibitors. Surfactant inhibitors have many advantages such as, for example, high inhibition efficiency, low price, low toxicity, and easy production.<sup>21</sup>

Surfactants are molecules composed of polar hydrophilic group, the “head”, attached to a nonpolar hydrophobic group, the “tail”.<sup>22</sup> This unique molecular architecture leads to a rich spectrum of complex self-assembling phenomena when surfactants are dissolved in polar or non-polar solvents.<sup>23–25</sup> The adsorption behavior of surfactants at the solid/solution interface is somewhat similar to that at the gas/solution interface although the latter is more complicated than the former. It is reported that the interaction between hydrocarbon chains of surfactants will occur through van der Waals forces when the surface concentration of surfactant adsorbed on solid surface is high enough, forming an organized structure, the hemimicelle,<sup>22</sup> which can be expected to decrease the corrosion reactions by blocking the surface of metals and alloys. Few reports about using surfactants to inhibit metal corrosion were found although surfactants have been widely used in chemical and light industry.

In this article, it seemed interesting to proceed with a study of the corrosion inhibition of mild steel with some of synthesized complex surfactants in CO<sub>2</sub>-saturated brine at

temperature of 50 °C. The weight loss and linear polarization resistance corrosion rate (LPR corrosion rate) methods are used in this investigation to evaluate the inhibiting efficiency of the studied complex surfactants.

## MATERIAL AND METHODS

### Chemical Composition of Mild Steel Alloy

Electrodes are made of mild steel grade 080A15 and have an area of 4.55 cm<sup>2</sup>. The Chemical composition of mild steel used in this study was given in *Table 1*. The data was provided by European Corrosion Supplies Ltd and was confirmed by Energy dispersive X-ray fluorescence.

### Synthesis of Complex Surfactants

Sunflower oil was hydrolyzed with solution of 25% NaOH for 7 hours at 90 °C. This process yield in fatty acid sodium salt which is reacted with 37% HCl acid solution

for extracting the fatty acids. Based on prepared fatty acid the sulfating syntheses were performed. The Sulfating process was done in a 500 ml ground glass three-neck flask, equipped with a mechanical stirrer and a thermometer with a temperature controller. It was then charged with 100 gm fatty acid and 30 ml 10% sulfuric acid was also added drop by drop at the reaction temperature 75 °C with stirring for 7 hours. The product is sulfated fatty acid. The product was characterized by FT-IR spectroscopy (using a model FT-IR, Spectrum BX spectrometer using KBr disks) and physical-chemical methods (*Table 2*).

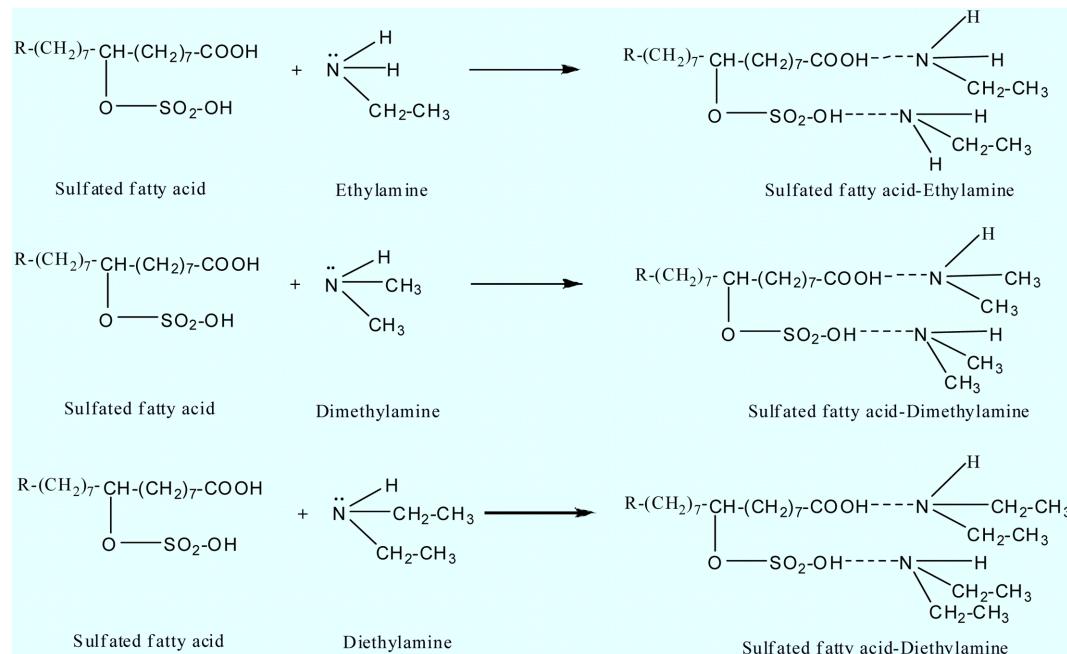
Sulfated fatty acid was taken at molar ratio 1:2 with ethylamine, dimethylamine or diethylamine. The components of reactions were mixed well for a period 30 min at 25 °C. The obtained complexes are generally viscous liquids. The synthesized surfactant complexes can be illustrated by *Scheme 1*. The chemical structure of the synthesized complex surfactants was characterized by physical-chemical spectro-

**Table 1.** Chemical composition of mild steel C1018

Element	Si	Ni	Cr	S	C	P	Mn	Fe
Content (wt%)	0.17	0.01	0.01	0.03	0.18	0.01	0.70	Balance

**Table 2.** Physical and chemical properties of fatty acid and sulfated fatty acid obtained from sunflower oil

Obtaining acid	Acid number mg KOH/g	Molecular weight gm mol <sup>-1</sup>	Iodine number 100 g iodine/g sample	Density, $d_{20}^2$ gm cm <sup>-3</sup>	Refraction, $\eta_{20}^D$
Fatty acid	145.6	279	112	0.907	1.4680
Sulfated fatty acid	280	377	—	0.901	1.4610



**Scheme 1.** Reactions Scheme of the Synthesis of surfactants Complexes.

**Table 3.** Some physico-chemical characteristics of synthesized surfactant complexes

Code number of the inhibitor	Name and abbreviation	External view of the complex	Base number mg HCl /g	Solubility of the complexes	Density, $d_4^{20}$ gm cm <sup>-3</sup>	M.wt gm mol <sup>-1</sup>
I	Sulfated fatty acid-Ethylamine complex (SFAEA)	Light Brown (Viscous)	0.89	Readily soluble in isopropyl alcohol, Readily soluble in mixture from water: isopropyl alcohol 70:30	0.971	431
II	Sulfated fatty acid-Dimethylamine complex (SFADMA)	Yellowish-brown (Very viscous)	1.03	Readily soluble in isopropyl alcohol, Readily soluble in mixture from water: isopropyl alcohol 70:30	0.979	431
III	Sulfated fatty acid-Diethylamine complex (SFADEA)	Brown (Viscous)	1.38	Readily soluble in water, isopropyl alcohol	0.988	487

scopic methods (*Table 3*). Infrared spectra for the synthesized complexes were measured using a model FT-IR, Spectrum BX spectrometer using KBr disks.

### Corrosion Inhibition Test

The aggressive solution, 1% NaCl, was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was from 25 to 150 ppm used for corrosion measurements. All solutions were prepared using a mixture from distilled water and isopropyl alcohol in a ratio 70:30.

### Corrosion Measurements

To study the corrosion protection ability of the synthesized surfactants, one of the newest devices in recent years ACM, GILL AC was used. The apparatus consists of a personal computer HP Pavilion (monitor, CPU), a Potentiostat/Galvanostat model ACM GILL AC (UK), four pieces of glasses with a capacity of 4000 ml, electrodes, CO<sub>2</sub> tank and installations-regulating the quantity fed CO<sub>2</sub>. A magnetic stirrer stirred the prepared 1% of the sodium chloride solution for 30 minutes in 4 L beaker. The prepared solution poured into the four glass beakers (1000 ml for each one). These beakers were, then placed on a heater at 50 °C for 1 hour under a pressure of 0.9 bars carbon dioxide saturated the solution. The electrodes were immersed in the medium and are connected through a potentiometer ACM GILL AC. The surfaces of working electrode were cleaned by acetone before using. Electrodes are used for one time only. After 1 hour, except for one beaker, the remaining three were fed with the suitable amount of inhibitor and continued supply of CO<sub>2</sub> under 0.9 bar pressure till the end of the experiment.

A Core Running program (Version 5.1.3.) varied the potential of the working electrode through a potentiometer ACM instruments Gill AC. Gill AC technology allows measuring DC and AC signals using standard Sequencer soft-

ware. A small sweep from typically, -10 mV to +10 mV, at 10 mV min<sup>-1</sup> around the rest potential is performed. The Core Running program converts a corrosion current in mA cm<sup>-2</sup> to different relationships (building on the corrosion rate *per* time (mm year<sup>-1</sup>), the metal loss *per* time (mg h<sup>-1</sup>).

Each experiment was performed with freshly prepared solution and clean set of electrodes. Measurements were conducted at temperature 50 °C for the investigated NaCl solution. For this purpose, magnetic stirrer with heater (115 V, 50/60 Hz) was used.

### Surface Tension Measurements

The surface tensions were determined by DuNouy Tensiometer, Kruss Type 8451 and the temperature was maintained precisely at 20 °C. Critical micelle concentration (CMC) values of surfactants were determined, according to the break points in plots of the surface tension versus log molar concentration of investigated surfactants.

### Surface Characterization

In order to observe any changes in surface morphologies of the mild steel samples after testing, the specimens were first immersed in the test media with and without an inhibitor for 4 days, then cleaned with bi-distilled water and acetone, and dried with cool air. Then the morphology of the tested sample was observed by using HORIBA XGT-7000 - Energy dispersive X-ray fluorescence (EDRF), a microscope with a system of partial/complete evacuation of the sample.

## RESULTS AND DISCUSSIONS

### Chemical Structure of the Synthesized Surfactants

**FT-IR:** The structural characteristics of purified products of synthesized acids based on sunflower oil (fatty acid and sulfated fatty acid) were confirmed by FT-IR spectroscopy in the range 4000–500 cm<sup>-1</sup>. The peaks of

fatty acid are in accordance with the characteristic peaks of fatty acid reported in the literatures.<sup>26</sup> The peak at about  $1709\text{ cm}^{-1}$  is due to the C=O carbonyl group of the carboxylic group, whereas the peak at  $1550\text{ cm}^{-1}$  arises due to C=C bond. This bond was broken after sulfating process. The peak at  $1377\text{ cm}^{-1}$  is due to S–O stretching absorption bands. It indicates the almost complete removal of C=C bond by sulfating process.

The chemical structures for surfactant complexes were recorded in FT-IR. The FT-IR absorption spectra showed an absorption band at the  $2335\text{--}2356\text{ cm}^{-1}$  region for all prepared complexes, indicating that the amine band was disappearing by emerging ammonium ion ( $\text{R}-\text{N}^+\text{H}_3$ ). In addition, there was a strong band at  $850\text{--}900\text{ cm}^{-1}$ , indicating the presence of multiple ( $\text{CH}_2$ ) groups. The very strong bands at the  $2852\text{--}2865\text{ cm}^{-1}$  region for all the prepared complexes were due mainly to the methyl asymmetric stretching vibration. The sharp band at  $2925\text{--}2968\text{ cm}^{-1}$  was observed for all prepared complexes due to the stretching vibration of the symmetric methylene group. The strong band at  $1720\text{--}1732\text{ cm}^{-1}$  for all compounds indicating to the increasing C=O group frequency due to occurring a link between the acid proton with the amino nitrogen that leads to increasing the attraction of electrons from carbonyl group. The FT-IR absorption spectra confirmed that the disappearance of –OH band of acid (broad band), this confirmed the transfer of proton of acid to nitrogen atom of amine to form  $-\text{NH}_3^+$  group. The results are generally in agreement with the expected correlations.

**Physico-chemical measurements of the synthesized complex surfactants:** The physico-chemical properties of the synthesized complex surfactants were measured such as solubility, density and base number. From Table 2, it noted that the obtained complexes are generally viscous liquids. Their colors vary from light brown to brown color. The base numbers for all complexes were measured. The base number of SFADEA more than those of SFADMA and SFAEA. The base number of the investigated surfactants was increased in the following order: SFADEA (1.38) > SFADMA (1.03) > SFAEA (0.89).

### Weight Loss Measurements

The weight loss of mild steel in  $\text{CO}_2$ -saturated solution in the presence of 100 ppm of different synthesized complex surfactants as chemical inhibitors at  $50^\circ\text{C}$  is measured and plotted in Fig. 1. From this figure we notice that, the weight loss decrease in the presence of studied inhibitors, and then it gives a constant value.

As the results the surface coverage ( $\theta$ ) of compounds is

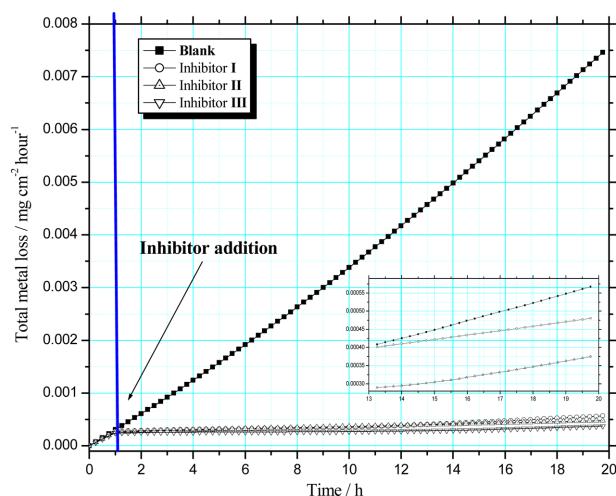


Fig. 1. Weight loss-time curves for mild steel dissolution in  $\text{CO}_2$ -saturated brine in the absence and presence of 100 ppm of different inhibitors at  $50^\circ\text{C}$ .

increasing more clearly. This surface coverage ( $\theta$ ) is calculated using the following equation:

$$\theta = \frac{W_0 - W_i}{W_0} \quad (1)$$

Where  $W_0$  and  $W_i$  are the weight losses per unit area in the absence and presence of the inhibitor, respectively. The percentage inhibition efficiency, ( $IE$  %), of the surfactants is calculated by applying the following equation:<sup>27</sup>

$$IE, \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

The data in Fig. 2 shows that, the inhibition efficiency

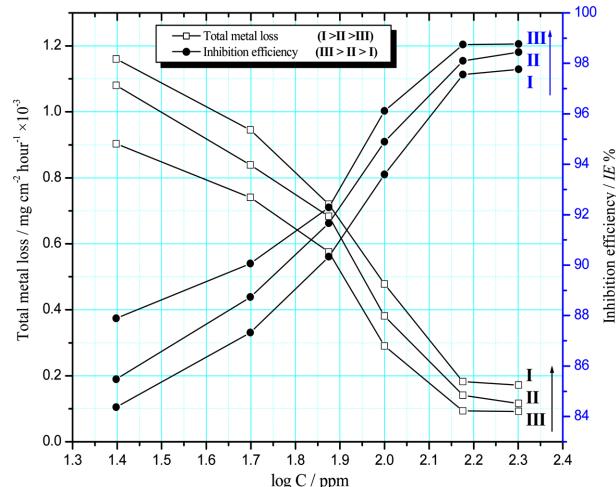


Fig. 2. Dependence of inhibition efficiency and weight loss of mild steel on the concentrations of inhibitors in  $\text{CO}_2$ -saturated brine at  $50^\circ\text{C}$ .

increased and weight loss decreased with the increase of surfactant concentration. Hence, the weight loss was a concentration dependent. In Fig. 2, it is obvious that the corrosive loss masses of mild steel sample decreases and inhibition efficiency increases with increasing the concentrations of complex surfactants in CO<sub>2</sub>-saturated solution, suggesting that studied complex surfactants are efficient corrosion inhibitors for mild steel in CO<sub>2</sub>-saturated brine. The protective action of studied inhibitors during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film isolates the metal surface from the corrosive medium.<sup>28</sup>

The highest inhibition efficiencies are observed when the concentrations of surfactants (150 ppm) reach values close to its critical micellar concentration (CMC) (159, 153 and 147 ppm for surfactants **I**, **II** and **III**, respectively) (see Fig. 3). As the concentration of surfactant molecules approaches the CMC, micelles form in solution, and similar aggregate structures such as bilayers and multilayers form on the surface. Further increase in surfactant concentration above the CMC results in other types of aggregates such as lamellar structures and rod-like micelles that can form in solution as well as analogous bilayers or multilayers that form at interfaces.<sup>29,30</sup>

Consequently, in the context of corrosion inhibition using surfactants, the CMC marks an effective boundary condition below which surfactant adsorption is typically below the monolayer level, and above which adsorption can consist of multiple layers of adsorbed surfactant molecules. Above the CMC, increasing surfactant concentration leads to the gradual formation of multilayers that further reduce the

rate of corrosion.<sup>30</sup>

The average weight loss, the inhibition efficiencies and the surface coverage rates are found to depend on the concentrations of the inhibitors. The average weight loss is decreased, and the inhibition efficiencies and the surface coverage rates are increased with the increase of the surfactants concentrations. However, no appreciable decrease in weight loss, and increase in *IE*, % and  $\theta$  are noticed above certain concentrations which close to the critical micellar concentration (CMC) of studied surfactants (Fig. 2). This indicates that the inhibitory action of complex surfactants against mild steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limits the dissolution of mild steel, and the adsorption amounts of surfactants on steel increase with concentrations in the corrosive solutions. When the concentrations exceed certain values which are near the critical micelle concentrations of the complex surfactants, the adsorption amount of surfactants are close to the saturated conditions, therefore, the values of weight loss, *IE*, % and  $\theta$  are almost unchanged above these concentrations.

It can be inferred from the data shown in Fig. 2 that, the inhibition efficacy becomes nearly constant starting from 150 ppm. This concentration will be used as the up limit through this study. Conclusively, the surfactants inhibitors, having near unity  $\theta$ , was considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of mild steel significantly.

### LPR Corrosion Rate

The linear-polarization-resistance (LPR) corrosion rate bubble-test method involves evaluating the corrosion of a given metal in simulated brine saturated with CO<sub>2</sub> at a temperature equivalent to that in the field. During the test, CO<sub>2</sub> gas is sparged continuously into the test solution. The rate of corrosion is determined instantaneously with the LPR corrosion rate technique, in which a small direct-current voltage is applied to a pair of identical electrodes and the resultant current is measured.

Fig. 4a, b and c shows that, the change in corrosion rate (CR) with time for mild steel in CO<sub>2</sub>-saturated 1%NaCl solution containing different concentrations form inhibitors **I**, **II** and **III** at 50 °C. The inhibitor was added after 1 hour of exposure because at this time the corrosion potential got stable, allowing the measurement of the corrosion rate prior the injection of the inhibitor. The initial corrosion rate, without inhibitor, was measured to be between 2.59 and 3.784 mm y<sup>-1</sup>. It can be observed from Fig. 4 that the CR, in the absence of inhibitor, tends to

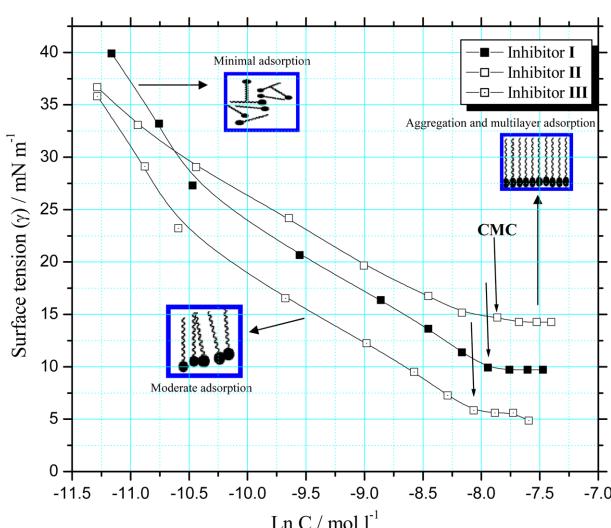
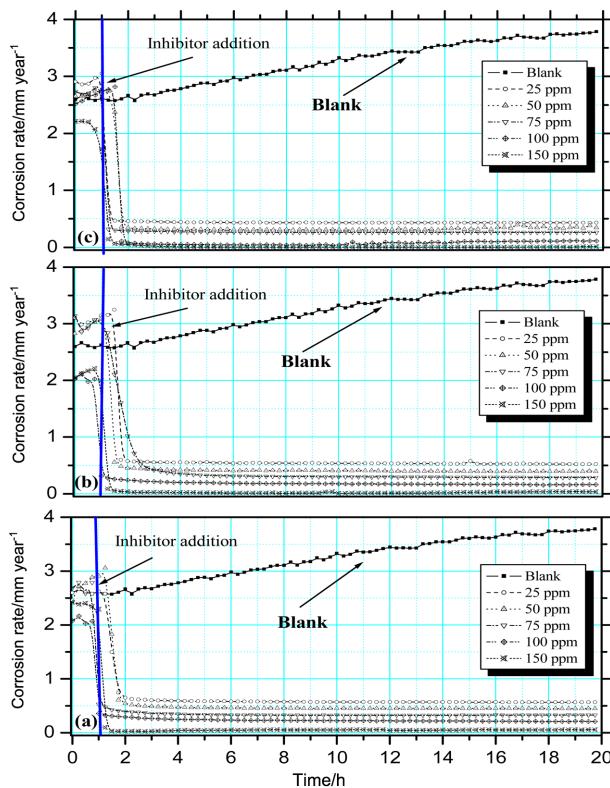


Fig. 3. Change of surface tension ( $\gamma$ ) with the concentration of the complexes surfactants at 293 K.



**Fig. 4.** Variation of the Corrosion rate with time for mild steel in  $\text{CO}_2$ -saturated brine containing different concentrations of (a) inhibitor I, (b) inhibitor II and (c) inhibitor III at  $50^\circ\text{C}$ .

increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite

( $\text{Fe}_3\text{C}$ ) which is part of the carbon steel.<sup>31</sup>

Variation of the corrosion rate for inhibitors I, II and III at different concentrations are presented in Fig. 4a, b and c. Corrosion parameters were calculated on the basis of LPR corrosion rate test. The inhibition efficiency ( $IE, \%$ ) and surface coverage ( $\theta$ ) were calculated according to the following equations:

$$IE, \% = \frac{CR_0 - CR_i}{CR_0} \times 100 \quad (3)$$

$$\text{Surface coverage } (\theta) = \theta = 1 - \frac{CR_i}{CR_0} \quad (4)$$

Where  $CR_0$  is the corrosion rate without inhibitor and  $CR_i$  the corrosion rate when inhibitor is present. It can be seen that the presence of inhibitors results a high decrease in the rate of corrosion. In the case of these inhibitors, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 98.51 and 99.72% at 150 ppm after 20 hour of exposure (Table 4). This trend may result from the fact that adsorption of these complex surfactants forms thin inhibitor films on the metal surface which in order relatively isolate the metal surface from the corrosive environment causing much reduced corrosion rates. Inhibition efficiency of these films depends on various factors including but not limited to corrosivity of the environment, concentration of the surfactant, any synergistic effects with other molecules present in the environment and/or flow/shear effects.<sup>32</sup>

**Table 4.** The corrosion parameters for mild steel electrode in  $\text{CO}_2$ -saturated brine in the absence and presence of various concentrations of complex surfactants at  $50^\circ\text{C}$

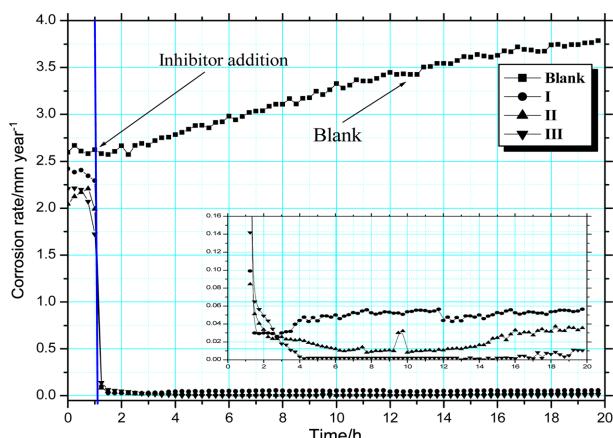
Inhibitors	Concentration ppm	Corrosion rate $\text{mm year}^{-1}$	Surface coverage $\theta$	The Inhibition Efficiency $IE\%$
<b>I</b>	CO <sub>2</sub> -saturated brine without inhibitor	0.0	3.784	—
	25	0.5657	0.8505	85.05
	50	0.4514	0.8807	88.07
	75	0.3305	0.9114	91.14
	100	0.2094	0.9446	94.46
	150	0.0563	0.9851	98.51
<b>II</b>	25	0.5226	0.8618	86.18
	50	0.3968	0.8951	89.51
	75	0.2838	0.9249	92.49
	100	0.1594	0.9578	95.78
	150	0.0354	0.9906	99.06
<b>III</b>	25	0.4297	0.8864	88.64
	50	0.3457	0.9086	90.86
	75	0.2597	0.9313	93.13
	100	0.1122	0.9703	97.03
	150	0.0104	0.9972	99.72

*Table 4* shows the calculated values of corrosion rates, the inhibition efficiencies and the surface coverage in the absence and presence of different concentrations of different inhibitors at 50 °C. The results show that the corrosion rate of mild steel in CO<sub>2</sub>-saturated solution decreased and the inhibition efficiencies are increased as the surfactant concentration increased. The corrosion rate dropped sharply when inhibitor was introduced. The drop in corrosion rate was significant when small concentrations were introduced (before 150 ppm). For concentration of 150 ppm and higher, the corrosion rate did not show any significant decrease and remained approximately constant. The value of inhibition efficiency was increased with increasing the inhibitor concentration, *Table 4*, indicating that a higher surface coverage was obtained in CO<sub>2</sub>-saturated brine with the optimum concentration of the inhibitor. This could be explained on the basis of inhibitor adsorption on the metal surface and the adsorption process enhances with increasing inhibitor concentration.<sup>33</sup>

*Fig. 5* shows the effect of different surfactants on the corrosion rate of mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing 100 ppm of inhibitors at 50 °C. This plot indicates that, the presence of different inhibitors decreases the rate of corrosion. However, the maximum decrease in the corrosion rate was observed for inhibitor (**III**) and the inhibition efficiency of the investigated inhibitors was increased in the following order: **III > II > I** (See section 3.5). LPR corrosion rate results showed the same trend which obtained from weight loss method.

#### Adsorption Isotherm and Thermodynamic Parameters for the Corrosion Process

The adsorption of the inhibitor on the metal surface



**Fig. 5.** Variation of the corrosion rate with time for mild steel in CO<sub>2</sub>-saturated brine containing 100 ppm from different inhibitors at 50 °C.

impedes the dissolution reaction. The metal surface in aqueous solution is always covered with adsorbed water molecules. Therefore, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process.<sup>34</sup> In inhibited solutions, the corrosion rate and the inhibitor efficiency depend on the type and number of active sites at metal surface, the charge density, the molecular size of the inhibitor, the metal–inhibitor interaction, and the metallic complex formation.<sup>35</sup>

The adsorption isotherm can give an insight into the adsorption process and the information on the metal–inhibitor interaction, and it can be derived from the curve of surface coverage rate against inhibitor concentration. The adsorption mechanism of complex surfactants involves two steps, as for conventional surfactants. The first step occurs at very low concentration and corresponds to a binding of individual surfactants on charged sites on the metal surface. The second step occurs at a concentration below the CMC and corresponds to the formation of surface aggregates.<sup>36</sup>

The surface coverage rates ( $\theta$ ) for different concentrations of the inhibitors in CO<sub>2</sub>-saturated 1%NaCl solution have been evaluated from LPR corrosion rate measurements. Several adsorption isotherms were attempted to fit  $\theta$  values to standard isotherms including that of Frumkin, Temkin, Freundlich and Langmuir isotherm. However, so far the best fit was obtained by assuming the Langmuir isotherm for studied complex surfactants absorbed on mild steel surface. This means the adsorption of complex surfactants on the metal surface in CO<sub>2</sub>-saturated solution is most likely the mono-layer adsorption as Langmuir model is described for monolayer adsorption.

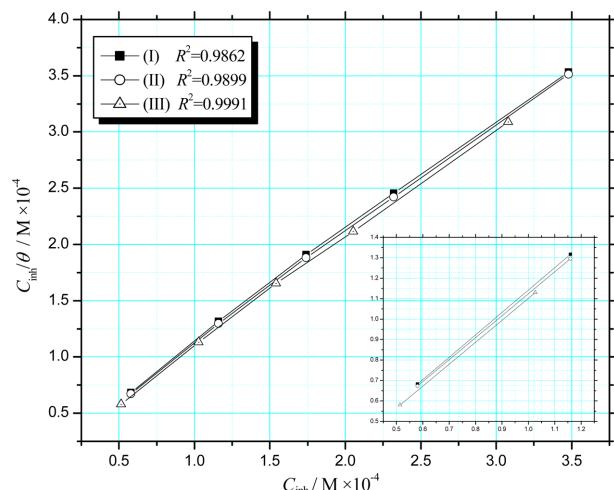
The Langmuir adsorption isotherm is described by the following equations:<sup>37</sup>

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \quad (5)$$

$C_{inh}$  is the inhibitor concentration,  $\theta$  is the surface covered and  $K_{ads}$  is the adsorption coefficient which is evaluated from the plots and is related to the standard free energy of adsorption,  $\Delta G_{ads}^o$  by:<sup>38</sup>

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right) \quad (6)$$

The surface coverage ( $\theta$ ) for various concentrations of the inhibitors in CO<sub>2</sub>-saturated brine has been evaluated from the LPR-corrosion rate measurements. *Fig. 6* shows the relationships of  $C_{inh}/\theta$  versus  $C_{inh}$  of the studied complex surfactants and the obtained plots of the inhibitors are



**Fig. 6.** Langmuir adsorption isotherm ( $C_{inh}/\theta$  vs.  $C_{inh}$ ) fitting of the obtained from LPR corrosion rate data for mild steel in  $\text{CO}_2$  saturated brine containing various concentrations of inhibitors at 50 °C.

**Table 5.** Thermodynamic parameters for the adsorption of the studied complex surfactants on mild steel electrode in  $\text{CO}_2$ -saturated brine

Inhibitors	Slope	Regression coefficients $R^2$	$K_{ads}$ $M^{-1} \times 10^4$	$\Delta G_{ads}^\circ$ kJ mol <sup>-1</sup>
I	1.05	0.9862	6.07	-44.61
II	1.08	0.9899	6.71	-45.01
III	1.02	0.9991	8.49	-47.25

linear with correlation coefficient  $R^2$  higher than 0.9862 (Table 5). This suggests that the adsorption of inhibitors on the mild steel surface in investigated media obeys the Langmuir adsorption isotherm. The calculated values of  $K_{ads}$  and  $\Delta G_{ads}^\circ$  are given in Table 5.

The high values of  $K_{ads}$  for studied complex surfactants indicate stronger adsorption on the mild steel surface in  $\text{CO}_2$ -saturated solution. It is also noted that, the high values of  $K_{ads}$  for inhibitor III indicate stronger adsorption on the mild steel surface than the inhibitors I, II. Large values of  $K_{ads}$  imply more efficient adsorption hence better inhibition efficiency.<sup>39</sup> The large value of  $K_{ads}$  obtained for the investigated surfactants agree with the high inhibition efficiency obtained.

The negative values of  $\Delta G_{ads}^\circ$  indicate the inhibitors are spontaneously adsorbed on the mild steel surface.<sup>36</sup> It is generally accepted that the values of  $\Delta G_{ads}^\circ$  up to -20 kJ mol<sup>-1</sup>, the types of adsorption are regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol<sup>-1</sup> or smaller, are seen

as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond.<sup>40,41</sup> It is clear from Table 5 that the values of  $\Delta G_{ads}^\circ$  in our measurements range from -44.61 to -47.25 kJ mol<sup>-1</sup>. These results indicate that the adsorption mechanism of complex surfactants on mild steel in  $\text{CO}_2$  saturated brine is typical chemisorption at the studied temperature. Chemisorption of the surfactant molecules could occur due to the formation of links between the d orbital of iron atoms, involving the displacement of water molecules from the metal surface, and the lone sp<sup>2</sup> electron pairs present on the N, S and/or O atoms of the inhibitor.

### Mechanism of Inhibition

The possible explanation of the inhibition is due to adsorption process which is considered as the key of the mechanism of inhibition action. It might be suggested that the surfactant molecules adhere to the steel surface. This leads to a decrease of the surface area at which cathodic and anodic reactions take place. Inhibition efficiency of the inhibitors compounds depends on many factors,<sup>42</sup> which include the number of adsorption active centers in the molecule and their charge density, molecular size, and mode of interaction with metal surface.<sup>35</sup> The transition of metal/solution interface from a state of active dissolution to the passive state of great interest. The inhibition effect by surfactants is attributed to the adsorption of the surfactant molecules via their functional group onto the metal surface. The adsorption rate is usually rapid and hence the reactive metal is shielded from the aggressive environment. At the same inhibitor concentration, the order of increasing inhibition efficiency of these tested complex surfactants are: III > II > I. Due to the following reasons:

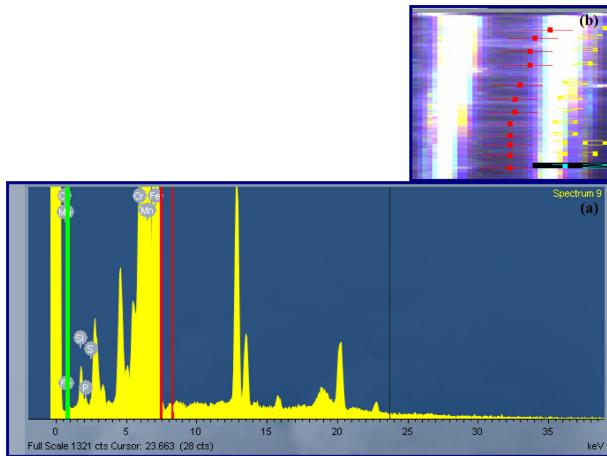
- The values of base number for the inhibitor I, inhibitor II, inhibitor III are 0.89, 1.03 and 1.38, respectively. From these values it is clear that the basicity increases and hence inhibition efficiency of these compounds increases in the order: III > II > I. The increases of the basicity of surfactants increase its proton affinity and charge. Thus by making suitable substitutions in the parent inhibitor molecule an improvement in the degree of corrosion inhibition was achieved.

- In the literature,<sup>42,43</sup> the IE% values of inhibitors depend on the molecular size. The IE% values of inhibitor III are higher than those of inhibitors II and I, due to the larger molecular size of the former compared with that of the latter. Fouda et al.<sup>43</sup> stated that the inhibition efficiency of Al by thiosemicarbazide derivatives in 2-N HCl solution

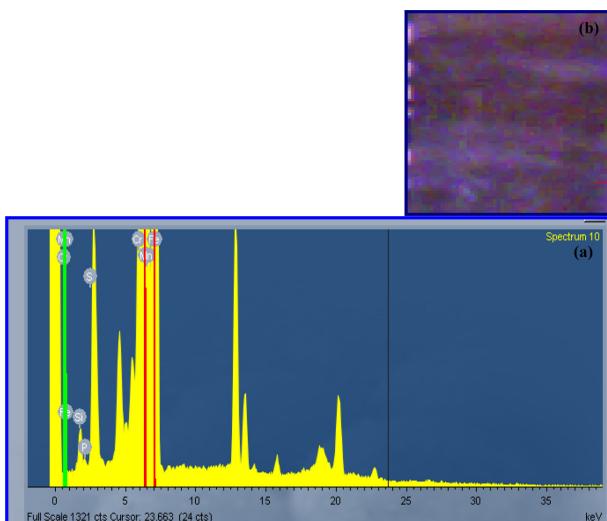
depend on molecular size of inhibitor. The molecular weight of the inhibitor has a direct influence on its inhibition efficiency. The increase in molecular weight of the inhibitor is due to an increase in the length of the hydrocarbon chain of compound. The rise of the inhibition efficiency is due to the inductive effect of the methyl groups.

### Surface Characterization

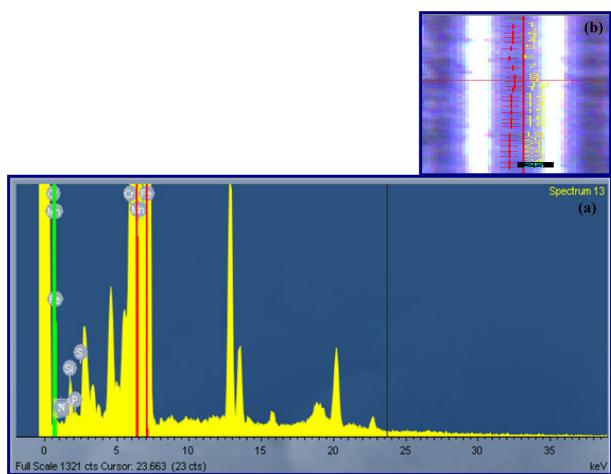
*Fig. 7a* shows an EDRF spectroscopy for mild steel surface. The characteristics peaks are related to metals present in the alloy. In the absence of inhibitors, *Fig. 8a* exhibits the characteristics peaks are related to Fe, Mn, P, Cr and oxygen elements. This indicated that the corrosion product on mild steel surface being metal oxide. However, the data in



**Fig. 7.** EDRF analysis of mild steel electrode surface before study (a) and the picture of mild steel electrode surface (b).



**Fig. 8.** EDRF analysis of mild steel electrode surface after immersion in CO<sub>2</sub>-saturated solution for 4 days without inhibitors (a) and the picture at the same conditions (b).



**Fig. 9.** EDRF analysis of mild steel electrode surface after immersion in CO<sub>2</sub>-saturated solution containing 150 ppm inhibitor **III** for 4 days (a) and the picture at the same conditions (b).

*Fig. 9a* in the presence of 150 ppm of inhibitor **III** shows additional peaks characteristic of N element, and the lower peaks height of Fe than those observed in the absence of inhibitors. This result proved that the adsorption of inhibitor molecule on mild steel surface leads to a decrease of metal oxide layer, and higher concentration of the inhibitor is necessary to delay the corrosion process.

*Fig. 7b* shows image of mild steel surface. The picture shows the brightness of the electrode surface without any inclusions. *Figs. 8b, 9b* show the picture of the passive film formed on the mild steel surface after immersion in CO<sub>2</sub>-saturated brine for 4 days in the absence and presence of inhibitor **III**. In the absence of inhibitor (*Fig. 8b*), the results exhibited that thick porous layer of corrosion product (oxide film) covered all electrode surface; the surface was strongly damaged, so that the electrode surface can not be seen. While *Fig. 9b* shows the image of the electrode surface in presence of 150 ppm of the inhibitor **III**. The image reveal that, the surface is almost free from damages and it is smooth, which indicates a good protective film present on the mild steel surface and also confirms the highest inhibition efficiency of the prepared complex surfactants.

### CONCLUSIONS

Weight loss and LPR corrosion rate are used to study corrosion of mild steel in CO<sub>2</sub>-saturated 1%NaCl solution and the inhibiting effect of three complex surfactants synthesized based on sunflower oil and nitrogen containing compounds. The data obtained from all the used methods

are in good agreement with each other. The results showed that, all studied compounds act as effective inhibitors in the investigated medium. The highest inhibition efficiency is obtained by inhibitor **III** (99.72% at 150 ppm).

Analysis of the obtained data show that, the inhibiting properties increase with inhibitor concentration. Maximum inhibition efficiency of the surfactants is observed at concentrations around its critical micellar concentration (CMC). The inhibition efficiency increases in accordance to the order: **III > II > I** for all concentrations. Higher molecular size of inhibitors and high electron density on the adsorption centers are responsible for high corrosion efficiency.

It is found that the inhibition occurs through adsorption, which obeys the Langmuir adsorption isotherm. Calculated Gibbs free energy of adsorption ( $\Delta G_{ads}^o$ ) confirms the chemical nature of the adsorption. Energy dispersive X-ray fluorescence microscopy observations of the electrode surface showed that a surface film of inhibitor is formed on the electrode surface.

**Acknowledgments.** The authors would like to thank the Institute of Petrochemical Processes- Azerbaijan National Academy of Sciences for support this work and Egyptian Ministry of Higher Education - sector missions for the financial support.

## REFERENCES

- El-Sayed, A.; Mohran, H. S., Abd El-Lateef, H. M. *Monatsh Chem.* **2012**, *143*, 51.
- Ahamad, I.; Quraishi, M. A. *Corros. Sci.* **2009**, *51*, 2006.
- Obot, I. B.; Obi-Egbedi, N. O. *Corros. Sci.* **2010**, *52*, 198.
- Popova, A.; Sokolova, E.; Raicheva, S.; Christov, M. *Corros. Sci.* **2003**, *45*, 33.
- Shukla, S. K.; Quraishi, M. A. *Corros. Sci.* **2009**, *51*, 1990.
- Behpour, M.; Ghoreishi, S. M.; Soltani, N.; Salavati-Niasari, M.; Hamadanian, M.; Gandomi, A. *Corros. Sci.* **2008**, *50*, 2172.
- Qiu, L.; Wu, Y.; Wang, Y.; Jiang, X. *Corros. Sci.* **2008**, *50*, 576.
- Hosseini, S. M. A.; Azimi, A. *Corros. Sci.* **2009**, *51*, 728.
- Hosseni, M.; Mertens, S. F. L.; Ghorbanifar, M.; Arshadi, A. R. *Mater. Chem. Phys.* **2003**, *78*, 800.
- Bentiss, F.; Lebrini, M.; Vezin, H.; Lagrenée, M. *Mater. Chem. Phys.* **2004**, *87*, 18.
- Benali, O.; Larabi, L.; Tabti, B.; Harek, Y. *Anti-Corros. Method Mater.* **2005**, *52*, 280.
- Li, D. G.; Feng, Y. R.; Bai, Z. Q.; Zheng, M. S. *App. Surf. Sci.* **2007**, *253*(20), 8371.
- Li, T.; Yang, Y.; Gao, K.; Lu, M. *J. Univ. Sci. Technol. B., Mineral, Metallurgy, Material* **2008**, *15*(6), 702.
- Lopez, D. A.; Simison, S. N.; de Sanchez, S. R. *Corros. Sci.* **2005**, *47*(3), 735.
- Nesic, S.; Postlethwaite, J.; Olsen, S. *Corrosion* **1996**, *52*(4), 280.
- Sun, M.; Nesic, S. *Corrosion* **2008**, *64*(4), 334.
- Sun, W.; Nesic, S.; Papavinam, S. *Corrosion* **2008**, *64*(7), 586.
- Wang, F.; Postlethwaite, J. *CORROSION/2001*, Paper No. 41 (Houston, TX: NACE, 2001).
- Abd El-Lateef, H. M.; Abbasov, V. M.; Aliyeva, L. I.; Ahmedov, N. S. *Petrochemistry and oil Refining* **2011**, *12*, *4*(48), 231.
- Abd El-Lateef, H. M.; Aliyeva, L. I.; Abbasov, V. M.; Ismayilov, I. T.; Ismayilova, X. R. *Chemistry J.* **2012**, *2*, 51.
- Fuchs-Godec, R.; Doleček, V.; *Colloids Surf., A* **2004**, *244*, 73.
- Bastidas, J. M.; Pinilla, P.; Polo, J. L.; Miguel, S. *Corros. Sci.* **2003**, *45*, 427.
- Bolzán, A. E.; Wakenge, I. B.; Piatti, R. C. V.; Salvarezza, R. C.; Arvia, A. J. *J. Electroanal. Chem.* **2001**, *501*, 241.
- Stipnišek-Lisac, E.; Gazivoda, A.; Madžarac, M. *Electrochim. Acta* **2002**, *47*, 4189.
- Sahin, M.; Bilgic, S.; Yilmaz, H. *Appl. Surf. Sci.* **2002**, *195*, 1.
- Alberta Aryee, N. A.; Frederik, R.; de Voort, V.; Simpson, B. K. *Process Biochem.* **2009**, *44*, 401.
- Singh, A.; Singh, V. K.; Quraishi, M. A. *Rasayan J. Chem.* **2010**, *3*, 811.
- Oguzie, E. E. *Corros. Sci.* **2007**, *49*, 1527.
- Interfacial Phenomena in Apolar Media; Surfactant Science Series*, Vol. 21, Marcel Dekker Inc.: New York, 1987, p 166.
- Abd El-Lateef, H. M.; Aliyeva, L. I.; Abbasov, V. M.; Ismayilov, T. I. *Adv. App. Sci. Res.* **2012**, *3*(2), 1185.
- Farelas, F.; Ramirez, A. *Int. J. Electrochem. Sci.* **2010**, *5*, 797.
- Ibrahim, T. H.; Abou Zour, M. *Int. J. Electrochem. Sci.* **2011**, *6*, 6442.
- Zhang, Z.; Chen, S.; Li, Y.; Li, S.; Wang, L. *Corros. Sci.* **2009**, *51*, 291.
- Chauhan, L. R.; Gunasekaran, G. *Corros. Sci.* **2007**, *49*, 1143.
- Avci, G. *Colloids Surf., A* **2008**, *317*, 730.
- Qi Zhang; Zhinong Gao; Feng Xu; Xia Zou; *Colloids Surf., A* **2011**, *380*, 191.
- Khaled, K. F.; Al-Qahtani, M. M. *Mater. Chem. Phys.* **2009**, *113*, 150.
- Sahin, M. S.; Bilgic; Yilmaz, H. *Appl. Surf. Sci.* **2002**, *195*, 1.
- Refay, S. A.; Taha, F.; Abd El-Malak, A. M. *Appl. Surf. Sci.* **2004**, *236*, 175.
- Branzoi, V.; Branzoi, F.; Baibarac, M. *Mater. Chem. Phys.* **2000**, *65*, 288.
- Yurt, A.; Ulutas, S.; Dal, H. *Appl. Surf. Sci.* **2006**, *253*, 919.
- Fouda, A. S.; Abdallah, M.; Ahmed, I. S.; Eissa, M. *Arabian Journal of Chemistry*, in press, 2010.
- Fouda, A. S.; Moussa, M. N.; Taha, F. I.; Elneanaa, A. I. *Corros. Sci.* **1986**, *26*, 719.