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## **Adsorption and Corrosion Inhibitive Properties of Novel Surfactants in the Series of Fatty Acids Based on Palm Oil on Carbon Steel in CO<sub>2</sub>-containing Solution**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors contributed in practical work and managed the analysis of the study. All authors read and approved the final manuscript.*

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### **ABSTRACT**

Some novel surfactants in the series of fatty acids were synthesized based on palm oil. The inhibition efficiency ( $\eta$  %) of these surfactants has been studied by linear polarization corrosion rate and potentiodynamic polarization measurements in CO<sub>2</sub>-saturated brine at 50°C. A significant decrease in the corrosion rate was observed in the presence of the investigated inhibitors. The percentage inhibition efficiency ( $\eta$  %) increases by increasing the inhibitor concentration. Potentiostatic polarization curves indicate that, the inhibitors under investigation act as mixed type. Tafel slopes are approximately constant and independent on the inhibitor concentration. The inhibition of carbon steel corrosion is due to the adsorption of the inhibitor molecules on the surface, which follows Langmuir adsorption isotherm. The changes in the surface morphology

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and composition of carbon steel samples with corrosion inhibitors were examined using Energy dispersive X-ray fluorescence (EDRF).

*Keywords: Carbon steel; palm oil; surfactants; inhibition; EDRF.*

## 1. INTRODUCTION

A wide range of liquids are extracted from oil and gas fields to meet the increasing world energy demands. In addition to these liquids, compounds such as carbon dioxide, water and hydrogen sulphide are present naturally in gas wells. Carbon dioxide, apart from existing naturally in gas reservoirs is purposely injected into wells to enhance oil recovery. These compounds combine to form a corrosive environment at certain temperature, pressure, pH and concentration. Carbon dioxide (CO<sub>2</sub>) corrosion, also known as "sweet corrosion" is one of the major problems in oil and gas industry, costing billions of dollars every year [1]. 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 [2-8] and corrodes carbon, steel a primary construction material for pipelines in oil and gas industries. Therefore carbon dioxide corrosion has been of interest to researchers in oil industries for many years and there exists many theories about the mechanism of CO<sub>2</sub> corrosion [9,10].

Corrosion inhibitors are used to prevent metal dissolution and acid consumption [11]. Most organic inhibitors are substances with at least one functional group, which binds to the metal surface. These functional groups contain at least one heteroatom like nitrogen [12], phosphorus and sulfur [13,14]. Surfactants are special type of organic compounds and exhibit unique properties due to their amphiphilic structure, consisting of hydrophilic and hydrophobic molecular segments. They form hydrophobic barrier film as a result of the interaction of hydrophilic side with the metal surface, which prevents direct contact between metal surface and corrosive environment. The surfactant inhibitors have many advantages, such as being environmentally friendly, high efficiency, low price and availability [15–17]. Adsorption of surfactants on metal surface can markedly increase the corrosion-resistance [18] and therefore the study of the relationship between the adsorption and corrosion inhibition is of great importance.

The purpose of this study is to investigate the adsorption and corrosion inhibitive properties of newly synthesized surfactants from palm oil on carbon steel in CO<sub>2</sub> containing solution using linear polarization corrosion rate, potentiodynamic polarization and Energy dispersive X-ray fluorescence techniques.

## 2. MATERIALS AND METHODS

### 2.1 Materials: Butun ishletdiyiniz reaktivleri, onlari hardan aldighinizi burda yazin

#### 2.1.1 Metal electrodes

Electrodes were made of 080A15 carbon steel provided by European Corrosion Supplies Ltd. The manufacturer provided chemical composition is given in Table 1. The area of electrodes was 4.55 cm<sup>2</sup>.

**Table 1. Chemical composition of low carbon steel alloy**

Element	Si	Ni	Cr	C	S	P	Mn	Fe
Content, (wt. %)	0.24	0.01	0.10	0.18	0.05	0.05	0.50	Balance

**2.1.2 Synthesis of surfactants**

Palm oil was reacted with diethanolamine for 7 hours at 150-160°C, yielding fatty acid diethanolamine amide. The product was sulfated using. The product is sulfated fatty acid diethanolamine amide. Six types from surfactants were synthesized in high purity by the following compositions:  $(R-CH-(OSO_3M)-CON-(CH_2-CH_2-OH)_2)$  (where  $M= Na, K, NH_4, -NH-CH_2-CH_2-OH, -N-(CH_2-CH_2-OH)_2$  and  $-N(CH_3)_2$ ). List of the synthesized surfactants are shown in Table 2.

**Table 2. List of the synthesized surfactants**

Code number of the inhibitor, as used in the text	Name and abbreviation	Structure	molecular weight (g/mol)
I	Sodium salt of sulfated fatty acid diethanolamine amide (SS)		438
II	Potassium salt of sulfated fatty acid diethanolamine amide (PS)		454
III	Ammonium salt of sulfated fatty acid diethanolamine amide (AS)		432
IV	Sulfated fatty acid diethanolamine amide-monoethanolamine complex (MC)		465
V	Sulfated fatty acid diethanolamine amide-diethanolamine Complex (DC)		513
VI	Sulfated fatty acid diethanolamine amide-dimethylamine Complex (DM)		465

**2.1.3 Preparation of solutions**

1.0% aqueous NaCl solution was used as corrosive media. Synthesized surfactants were added at 25-100 ppm concentration range for corrosion measurements. Inhibitors were dissolved in water-alcohol mixture prior to adding into corrosion media.

## **2.1.4 Corrosion tests**

### *2.1.4.1 potentiodynamic polarization measurements*

Sodium chloride solution was placed in in 1000 ml cell and stirred for 60 min with magnetic stirrer. The cell was thermostated at 50°C for 1 hour under the pressure of 0.9 bars. Then solution was saturated with carbon dioxide. In order to remove any surface contamination and air oxidation byproducts, the working electrode was kept at -1500 mV (Ag/AgCl) for 5 min. Then cell was disconnected and shaken to remove adsorbed hydrogen bubbles from the electrode surface. Polarization measurements were performed on the rotating cylinder electrode (ACM Gill AC instrument connected to a personal computer) against Ag/AgCl reference electrode. The extrapolation of cathodic and anodic Tafel lines were carried out in a potential range  $\pm 100$  mV with respect to corrosion potential ( $E_{\text{corr}}$ ) at scan rate of 1 mV/s.

### *2.1.4.2 Linear polarization resistance (LPR) corrosion rate*

The LPR method is ideal for plant monitoring offering an almost instantaneous indication of corrosion rate, allowing for quick evaluation of remedial action and minimizing unscheduled downtime. 1% NaCl solution was stirred by magnetic stirrer for 60 min in 4000 ml beaker. Then solution was poured into the 4 glass beakers (1000 ml for each). These beakers with the solution were heated at 50°C for 1 hour under the pressure of 0.9 bars followed by saturation with carbon dioxide. Then, electrodes were placed into the medium and connected to the potentiometer (ACM GILL AC). The surface of the working electrodes was cleaned by acetone before using. After 1 hour, 3 beakers were fed with various amounts of the corrosion inhibitor under the continued supply of CO<sub>2</sub> and pressure of 0.9 bar until the end of the experiment as described in [15-16]. The remaining beaker was used as a blank.

The potential of the working electrode was varied by CoreRunning software (Version 5.1.3). This program also converts corrosion current density of mA/cm<sup>2</sup> to a corrosion rate in mm/year. A cylindrical 080A15 carbon steel rod was used as a working electrode. Both DC and AC signals were measured using standard Sequencer software. A small sweep from typically -10 mV to +10 mV at 10 mV/min around the rest potential was performed.

## **2.1.5 Surface characterization**

In order to observe changes in the surface morphologies of carbon steel, the specimens were first immersed in the test media with and without inhibitors for 3 days, then cleaned with double-distilled water and acetone, and dried with cool air. The morphology of the specimens was observed by using HORIBA XGT-7000-Energy dispersive X-ray fluorescence (EDRF) microscope with partial and complete evacuation of the sample.

## **2.1.6 Methods of evaluation of corrosion parameters**

Steady state open circuit corrosion potentials ( $E_{\text{corr}}$ ) of the electrodes were attained after 50–60 min of immersion into corrosive media with and without inhibitors. Corrosion current density ( $I_{\text{corr}}$ ) was determined by extrapolation of cathodic and anodic Tafel lines to corrosion potential ( $E_{\text{corr}}$ ) [19]. The inhibition efficiency expressed as percent inhibition ( $\eta\%$ ) is defined as:

$$\eta\% = \frac{I_{\text{uninh.}} - I_{\text{inh.}}}{I_{\text{uninh.}}} \times 100 \quad (1)$$

where  $I_{uninh.}$  and  $I_{inh.}$  are the uninhibited and inhibited corrosion currents, respectively. Tests were performed in CO<sub>2</sub>-saturated 1% NaCl solution.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 LPR Corrosion Rate and Corrosion Potential

LPR test has been performed in brine saturated with CO<sub>2</sub> at 50°C, in turbulent (convective is better) fluid stream for 20 hours. Fig. 1 shows the change in corrosion rate (CR) with time for carbon steel containing different concentrations of inhibitors (a) II, (b) VI and (c) V at 50°C. Inhibitors were added after 1 hour of exposure. This time is required for the stabilization of the corrosion potential, allowing the measurement of the CR prior the inhibitor injection. The initial CR without inhibitor was varied at 3.45 - 5.03mm y<sup>-1</sup> and reduced to 0.031 - 0.154mm y<sup>-1</sup> after injection of 100 ppm of the investigated inhibitors. CR in the absence of inhibitor tends to increase with time. This increase has been attributed to the galvanic effect between the ferrite and cementite (Fe<sub>3</sub>C) phases, existing in the original steel. Cementite accumulates on the surface after the preferential leaching of ferrite (α-Fe) as Fe<sup>2+</sup> [20,21], since Fe<sub>3</sub>C is known to be less active than the ferrite phase. Ferrite acts as anode while cementite acts as cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process [21-23].

Corrosion parameters for the inhibitors II, VI and V were calculated on the basis of LPR corrosion rate test (Fig. 1). The inhibition efficiency ( $\eta$  %) and surface coverage ( $\theta$ ) were calculated according to the following equations:

$$\eta\% = \frac{CR_0 - CR_i}{CR_0} \times 100 \quad (2)$$

$$\text{Surface coverage } (\theta) = \theta = 1 - \frac{CR_i}{CR_0} \quad (3)$$

where  $CR_i$  and  $CR_0$  are the corrosion rates with and without inhibitors, respectively. One can see that the injection of inhibitors significantly decrease the rate of corrosion. The corrosion rate decreases as the inhibitor concentration increases, reaching to maximum inhibition efficiency of 97.0 - 99.9 % at 100 ppm after 20 hrs of exposure (Table 3). This trend is believed to be due to the increase of the metal surface coverage with the increase in inhibitor concentration, forming effective barrier against the medium [21,24].

Table 3 shows the calculated values of corrosion rates, the inhibition efficiencies and the surface coverage with different concentrations of the inhibitors at 50°C. All these parameters were found to depend on concentrations of the inhibitors. The corrosion rates (CR) decreased, whereas inhibition efficiencies ( $\eta$  %) and the surface coverage values ( $\theta$ ) increased with the surfactant concentrations. This indicates that the inhibitory action against carbon steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limiting the dissolution of carbon steel. Amounts of the adsorbed surfactants increase with the increase of their concentration in the solution.

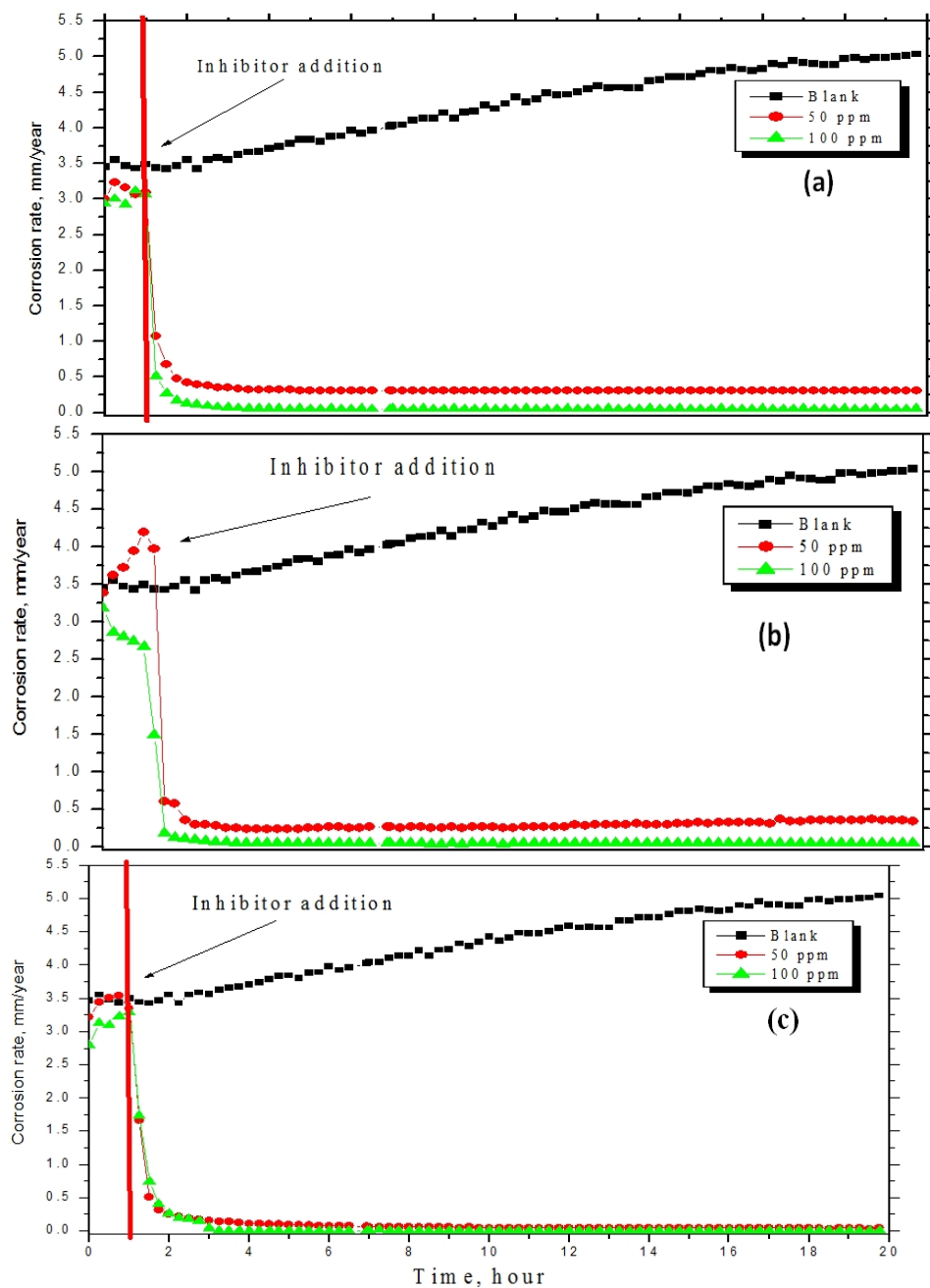


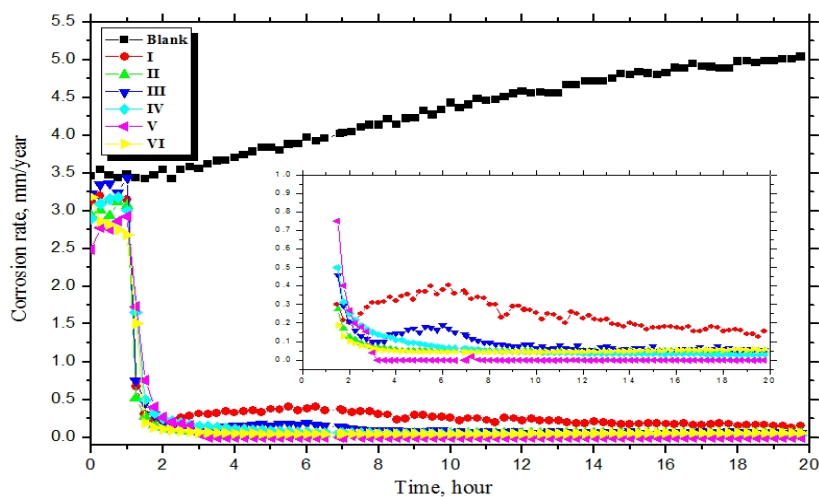
Fig. 1. Variation of the Corrosion rate with time at 50°C for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations of inhibitors (a) II, (b) VI and (c) V synthesized based on palm oil.

**Table 3. The corrosion parameters obtained from LPR corrosion rate measurements for carbon steel electrode in CO<sub>2</sub>-saturated brine in the absence and presence of**

Inhibitors code	Concentration, ppm	Corrosion rate (mm/year)	Surface coverage $\theta$	The inhibition efficiency, $\eta\%$
Absence	0.0	5.037	-----	-----
I	50	0.497	0.90	90.12
	100	0.154	0.97	97.00
II	50	0.308	0.93	93.88
	100	0.054	0.98	98.92
III	50	0.426	0.91	91.54
	100	0.056	0.98	98.88
IV	50	0.178	0.96	96.45
	100	0.031	0.99	99.40
V	50	0.031	0.99	99.38
	100	0.005	0.99	99.90
VI	50	0.336	0.93	93.32
	100	0.055	0.98	98.89

*Various concentrations of investigated surfactants at 50°C*

Variation of the carbon steel corrosion rate with time was measured in CO<sub>2</sub>-saturated brine containing 100 ppm of inhibitor at 50°C (Fig. 2). The maximum decrease in the corrosion rate was observed for inhibitor (V) with the inhibition efficiencies descending in the following order: V>IV>II>VI>III>I. The highest inhibition efficiency of inhibitors IV and V may be attributed to the higher electron density of their functional groups leading to easier bond formation, greater adsorption and consequently, higher inhibition [25].



**Fig. 2. Variation of the Corrosion rate with time for carbon steel in CO<sub>2</sub>-saturated 1% NaCl solution containing 100 ppm of different inhibitors at 50°C.**

The high inhibition efficiency obtained in CO<sub>2</sub>-saturated solution in the presence of studied inhibitors by all investigated methods can be attributed to the formation of a protective film of iron carbonate (FeCO<sub>3</sub>) as follows [26]:



The anodic dissolution of iron in carbonic acid solutions gives ferrous ions [26].



According to these processes, a corrosion layer was formed on the steel surface. The properties of the formed layers and its effect on the corrosion rate are important factors to take into account when studying the corrosion of steels in CO<sub>2</sub> environments. Ogundele and White suggested that, iron carbonate, FeCO<sub>3</sub>, may be important in the formation of protective layers on steel surface [27]. The formation of iron carbonate can be explained by using the following Eq. [28].



Anodic shift in  $E_{\text{corr}}$  was observed for carbon steel in the presence of inhibitor (V) (Fig. 3). This is characteristic for the anodic and mixed type inhibitors [29] and shift is due to the active sites blocking by inhibitors [30,31]. In the case of CO<sub>2</sub> corrosion the anodic and cathodic reactions are the oxidation of iron and the reduction of hydrogen, respectively [31]. Considering that the active sites on the metal surface are the same for both the reactions before inhibitor addition, then the shift in  $E_{\text{corr}}$  by the inhibitor is logical, because its adsorption modifies the surface and changes the anodic and cathodic reaction rates. The change in  $E_{\text{corr}}$  is proportional to the inhibitor efficiency. Higher efficiencies were observed when the change in  $E_{\text{corr}}$  was toward more noble values [18,31].

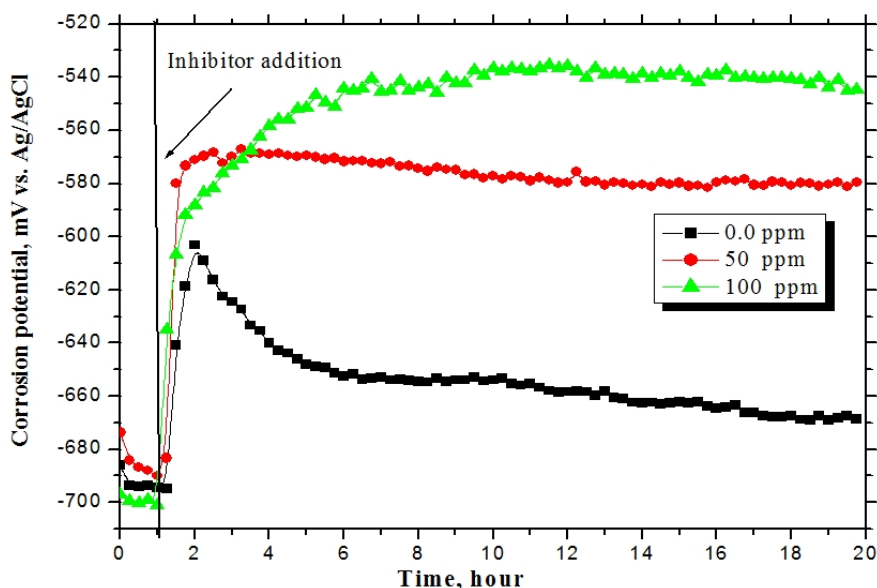


Fig. 3. Change in corrosion potential vs. time for carbon steel in CO<sub>2</sub>-saturated 1 % NaCl solution containing different concentrations from inhibitor V.



### 3.2 Potentiodynamic Polarization Measurements

The representative potentiodynamic polarization curves of carbon steel in CO<sub>2</sub>-saturated 1.0% NaCl solution with various concentrations of inhibitor V is shown in Fig. 4. Corrosion parameters were calculated on the basis of cathodic and anodic potential versus current density characteristics in the Tafel potential region. The values of the corrosion current density ( $I_{corr}$ ) for the investigated metal without and with the inhibitor were determined by the extrapolation of cathodic and anodic Tafel lines to the corrosion potential ( $E_{corr}$ ). Herein, the corrosion rates were calculated assuming that the whole surface of carbon steel is attacked by corrosion and no local corrosion is observed. The corrosion rates CR (mm year<sup>-1</sup>) from polarization were calculated using the following equation.

$$CR = \frac{I_{corr} \times t \times M}{F \times S \times d} \times 10 \quad (10)$$

where  $t$  is the time (s),  $M$  is the equivalent molar weight of iron (g mol<sup>-1</sup>),  $F$  is Faraday constant (96500 Cmol<sup>-1</sup>),  $S$  is the surface area of electrode,  $d$  is the density of iron, the constant 10 is used to convert the unit cm to mm.

As it can be clearly seen from Fig. 4 that, the addition of inhibitor V to the corrosive solution reduces both anodic dissolution of iron and cathodic hydrogen evolution reactions, as would be expected. The corrosion current density as well as corrosion rate of steel considerably reduced in the presence of the inhibitor. These results are indicative of the adsorption of inhibitor molecules on the carbon steel surface. The inhibition of both anodic and cathodic reactions is more pronounced with the increasing inhibitor concentration while the corrosion potential nearly remained the same relative to the corrosion potential observed with the blank solution. These results suggest that V can be classified as the mixed type corrosion inhibitor [32]. The similar behavior was observed after the addition of other surfactants to the CO<sub>2</sub>-saturated solution. It is also obvious that V has higher inhibition efficiency than the other inhibitors at a specified inhibitor concentration.

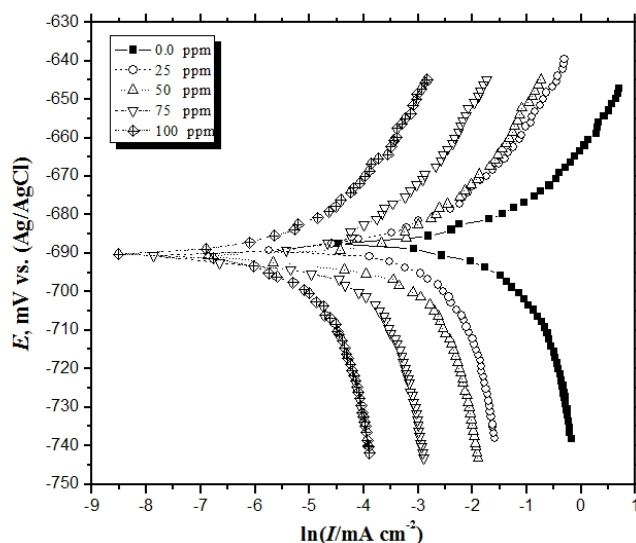


Fig. 4. Polarization plots of carbon steel electrode obtained in CO<sub>2</sub>-saturated brine containing different concentration of inhibitor (V) at 50°C

The electrochemical parameters,  $I_{corr}$ , inhibition efficiency ( $\eta$  %), anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ) obtained from the polarization measurements were listed in Table 4. The data exhibited that, the corrosion current density ( $I_{corr}$ ) decreases, and the inhibition efficiency ( $\eta$  %) increases as the concentration of inhibitors is increased. These results suggest that retardation of the electrode processes occurs, at both cathodic and anodic sites, as a result of coverage of these sites by surfactant molecules. However, the maximum decrease in  $I_{corr}$  was observed for (V). This may be attributed to the increase of the electron densities and the molecular size [33]. The increase of inhibitor efficiency with increasing the concentration can be interpreted on the basis of the adsorption amount and the coverage of surfactants molecules, increases with increasing concentration [34].

The fact that the slopes of the cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel lines in Table 4 are approximately constant and independent of inhibitor concentration indicate that these inhibitors act by simply blocking the available surface area. In other words, inhibitors decrease the surface area for corrosion of the investigated metal, and cause inactivation of a part of the surface with respect to corrosive medium [33]. The cathodic Tafel slopes ( $\beta_c$ ) are found to be greater than the respective anodic Tafel slopes ( $\beta_a$ ). These observations are correlated with the fact that the anodic exchange-current density values are less than those of the cathodic counter parts. It can be concluded that the overall kinetics of corrosion of carbon steel alloy in CO<sub>2</sub> saturated solution are under cathodic control [19,24].

Data in Table 4 shows that the inhibition efficiency increased with increasing the inhibitor concentrations. The inhibition efficiencies of the investigated inhibitors were increased in the following order: V>IV>II>VI>III>I. There was an increase in the efficiency of corrosion inhibition with increasing concentration, since the adsorption of C=O, oxygen, nitrogen and sulfur groups onto the metal surface was stronger and effectively protecting the surface. Conclusively, the surfactant inhibitor, having near unity  $\theta$  (Table 4) was considered as a good physical barrier shielding the corroding surface from corrosive medium and reducing the corrosion rate of carbon steel significantly. The inhibition efficiencies are in a good agreement with that calculated from LPR corrosion rate measurements.

The inhibition of carbon steel is attributed to the adsorption of surfactant molecules on the steel surface by the hydrophilic head groups. The hydrophobic chain may be oriented towards the aqueous medium and may be arranged horizontally to the steel surface.

### 3.3 Adsorption Isotherm Studies

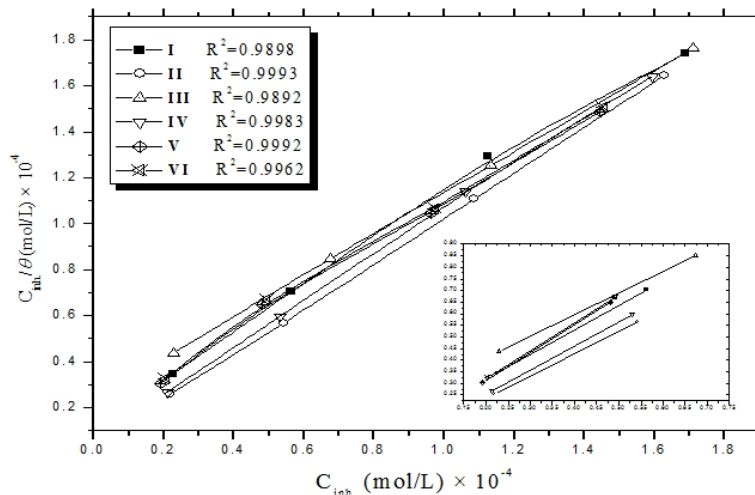
The degree of surface coverage ( $\theta$ ) for different inhibitor concentrations was evaluated from Potentiodynamic polarization measurements. The best correlation between the experimental results and isotherm functions was obtained at high inhibitor concentrations using the Langmuir adsorption isotherm. The Langmuir isotherm is given by the following equation [35]:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \quad (11)$$

where  $K_{ads}$  is the equilibrium constant of the inhibitor adsorption process and  $C_{inh}$  is the surfactant concentration. The plots of  $C_{inh}/\theta$  vs  $C_{inh}$  yielded straight lines with near unit slopes for all the surfactants showing that the adsorption model of these surfactants follows the Langmuir isotherm with good correlation (Fig. 5).

**Table 4. Corrosion parameters obtained from Tafel polarization for carbon steel in CO<sub>2</sub>-saturated 1% NaCl solution in the absence and presence of different concentrations of the prepared surfactants at 50°C.**

Inhibitors code	Conc. of inhibitor (ppm)	$i_{corr}$ (mAcm <sup>-2</sup> )	$\beta_a$ (mVdec <sup>-1</sup> )	CR (mm/year)	$-\beta_c$ (mVdec <sup>-1</sup> )	$\theta$	$\eta\%$
Absence	0.0	0.389	44	4.65	107	---	---
I	25	0.072	47	0.869	103	0.82	81.3
	50	0.044	39	0.534	105	0.86	88.5
	75	0.038	41	0.460	110	0.89	90.1
	100	0.016	44	0.199	108	0.97	95.7
II	25	0.052	42	0.627	107	0.84	86.5
	50	0.031	42	0.376	102	0.87	91.9
	75	0.014	46	0.172	106	0.91	96.3
	100	0.008	41	0.102	111	0.97	97.8
III	25	0.063	42	0.762	108	0.81	83.6
	50	0.038	48	0.460	106	0.85	90.1
	75	0.026	42	0.320	105	0.89	93.1
	100	0.010	40	0.130	102	0.97	97.2
IV	25	0.049	49	0.590	103	0.79	87.3
	50	0.021	46	0.251	110	0.84	94.6
	75	0.011	44	0.134	108	0.89	97.1
	100	0.004	40	0.055	107	0.95	98.8
V	25	0.041	39	0.497	103	0.67	89.3
	50	0.012	41	0.153	100	0.74	96.7
	75	0.009	44	0.111	103	0.82	97.6
	100	0.003	46	0.046	101	0.91	99.0
VI	25	0.057	46	0.688	105	0.73	85.2
	50	0.032	45	0.390	102	0.78	91.6
	75	0.023	41	0.283	103	0.84	93.9
	100	0.010	38	0.120	110	0.92	97.4



**Fig. 5. Curve fitting of the corrosion data obtained from Potentiodynamic polarization measurements for carbon steel in CO<sub>2</sub> saturated brine containing various concentrations of inhibitors according to Langmuir adsorption isotherm model at 50°C.**

The values of  $K_{ads}$  obtained from the Langmuir adsorption isotherm are listed in Table 5, together with the values of the Gibbs free energy of adsorption ( $\Delta G_{ads}^o$ ) calculated from [36]

$$K_{ads} = \frac{1}{C_{inh}} \times \frac{\theta}{1-\theta} \quad (12)$$

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \quad (13)$$

Where  $R$  is the universal gas constant,  $T$  is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution.

**Table 5. Thermodynamic parameters for the adsorption of the studied surfactants on carbon steel electrode in CO<sub>2</sub>- saturated brine.**

Inhibitors Code	Slope	Regression coefficients, $R^2$	$K_{ads}$ , $M^{-1} \times 10^5$	$\Delta G_{ads}^o$ ( $kJ mol^{-1}$ )
I	1.05	0.9898	2.01	-43.58
II	1.10	0.9993	2.87	-44.54
III	1.05	0.9892	2.23	-43.86
IV	1.04	0.9983	3.23	-44.81
V	1.03	0.9992	3.51	-44.86
VI	1.03	0.9962	2.76	-44.43

The high values of  $K_{ads}$  for studied surfactants indicate stronger adsorption on the carbon steel surface in CO<sub>2</sub>-saturated solution. It is also noted that, the high values of  $K_{ads}$  for surfactants V and IV indicate stronger adsorption on the carbon steel surface than the other surfactants (I, II, III and VI). This can be simply explained by the presence of additional donor atoms, such as oxygen, in the appended functional groups. Large values of  $K_{ads}$  imply more efficient adsorption and hence better inhibition efficiency [37]. The large value of  $K_{ads}$  obtained for the studied surfactants agree with the high inhibition efficiency obtained.

Generally, values of  $\Delta G_{ads}^o$  up to  $-20 kJ mol^{-1}$  are consistent with physisorption, while those around  $-40 kJ mol^{-1}$  or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [38,39]. In the present study, The values of  $\Delta G_{ads}^o$  obtained for studied surfactants on carbon steel in CO<sub>2</sub>-saturated solution ranges between  $-43.58$  and  $-44.86 kJ mol^{-1}$ , which are more than  $-40 kJ mol^{-1}$  (Table 5). These results indicate that the adsorption mechanism of surfactants on carbon steel in CO<sub>2</sub> saturated solution is typical chemisorption at the studied temperatures. 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  $sp^3$  electron pairs present on the N, S and/or O atoms of the inhibitors. These results were confirmed by FT-IR. The data for inhibitor I (SS) showed that, S=O stretching frequency drops from the level of  $1355 cm^{-1}$  to the level of  $1320 cm^{-1}$ . This suggests that electron cloud of S=O is shifted from S=O up to  $Fe^{+2}$  resulting in formation of  $Fe^{+2} -SS$  complex on metal surface. The high and negative values obtained for  $\Delta G_{ads}^o$  indicate that the adsorption process takes place spontaneously by strong interactions between the inhibitor and the steel surface, as was suggested by the obtained values of  $K_{ads}$ .

### 3.4 Surface Characterization

Figs. 6a and 7a show an EDRF spectroscopy for the carbon steel surface after immersed in CO<sub>2</sub>-saturated 1% NaCl solution without and with 100 ppm of inhibitor II for 3 days. In the absence of inhibitor, Fig. 6a exhibits the characteristics peaks which are related to Fe, Mn, P, Cr and oxygen elements. This indicated that the corrosion product on carbon steel surface being metal oxide and iron carbonate. However, the data in Fig. 7a in the presence of 100 ppm of inhibitor II show additional peak characteristic of K element, and the lower peaks height of Fe than those observed in the absence of inhibitors. These results proved that, the adsorption of inhibitor molecule on the carbon steel surface leads to decrease of oxide layer and to isolate the metal surface from the corrosive environment, causing much reduced in the corrosion rates.

The pictures of uninhibited and inhibited carbon steel surfaces are shown Figs. 6b and 7b. The morphology of the metal surface immersed in CO<sub>2</sub>-saturated brine (Fig. 6b) shows that the surface is rough, covered with corrosion products (FeCO<sub>3</sub> layer) and appearing to be full of pits and cavities. The surface was strongly damaged, so that the electrode surface can not be seen. The image of the carbon steel surface after immersion in CO<sub>2</sub>-saturated 1% NaCl solution with 100 ppm of inhibitor II is shown in Fig. 7b. The presence of the inhibitor leads to the formation of a protective layer adsorbed on the surface, which is responsible for the observed suppression of the rate of corrosion.

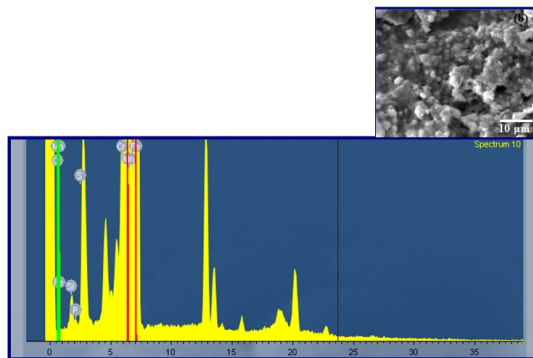


Fig. 6. EDRF analysis of carbon steel electrode surface after immersion in CO<sub>2</sub>-saturated solution for 3 days without inhibitor (a) and the picture at the same conditions (b)

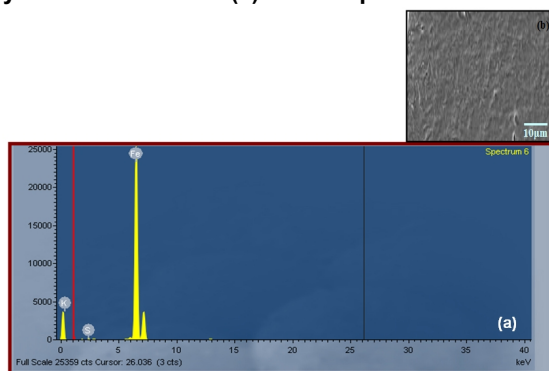


Fig. 7. EDRF analysis of carbon steel electrode surface after immersion in CO<sub>2</sub>-saturated solution containing 100 ppm of inhibitor II for 3 days (a) and the picture at the same conditions (b)

#### 4. CONCLUSION

Assessing the results of corrosion inhibition as well as the Surface characterization measurements led to the following conclusions:

- 1) Novel series of fatty acids surfactants were synthesized based on palm oil and diethanolamine.
- 2) The corrosion inhibition efficiencies of the synthesized surfactants were studied by linear polarization corrosion rate and Potentiodynamic polarization measurements, and they gave the same behavior. Test results show that the surfactants studied are efficient inhibitors for carbon corrosion in CO<sub>2</sub>-saturated brine solution.
- 3) The inhibition efficiencies increase with the increase of inhibitor concentrations. The maximum inhibition efficiency was observed for inhibitor V (99.90 % at 100 ppm) and the inhibition efficiency of the investigated surfactants was increased in the following order: V>IV>II>VI>III>I.
- 4) The surface coverage  $\theta$  was calculated on the basis of potentiodynamic polarization measurements and it was found that it can be fitted very well to the Langmuir isotherm.
- 5) The results of EDRF indicated that, the inhibitor molecules formed a good protective film on the carbon steel surface.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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