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A novel sulfated Fatty acid amides -based surfactants: synthesis and effect on the corrosion inhibition of carbon steel in CO₂-saturated 1% NaCl solution I. T. Ismayilov^{a, b}, Hany M. Abd El-Lateef^{a, c}*, V. M. Abbasov^a, L. I. Aliyeva^a, E. N. Efremenko^a, E. E. Qasimov^a, S. A. Mamedxanova^a

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ABSTRACT

The inhibition effect of some novel sulfated Fatty acid amides surfactants based on sunflower oil on the corrosion of carbon steel in CO₂-saturated NaCl solution has been studied at 50 °C by Tafel polarization and linear polarization resistance corrosion rate methods. The results showed that, all the investigated surfactants are good inhibitors even at low concentrations, and the inhibition efficiency (η %) increases with increased the inhibitor concentration. Adsorption of surfactants on the metal surface obeys the Langmuir adsorption isotherm model and was chemisorption. Polarization curves showed that, the studied surfactants are mixed-type inhibitors in CO₂-saturated brine. The results obtained from linear polarization resistance corrosion rate and polarizations are in good agreement. Energy dispersive X-ray fluorescence microscopy (EDRF) observations of the electrode surface confirmed the existence of such an adsorbed film.

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1. Introduction

Carbon steels are widely used in the oil and gas industry for numerous purposes. Though their corrosion resistance is limited, these materials are preferred to others due to economical reasons. One of the most frequent and aggressive environments found in the petroleum industry are fluids with high concentrations of chlorides containing carbon dioxide [1]. Carbon dioxide dissolved in water or aqueous solutions has been known to cause corrosion damage to a variety of steel technical equipment in oil and gas production industries [2–4]. In oil industry, CO_2 corrosion results from the water saturated with CO_2 containing chloride associated with the crude/gas production. In the last two decades the CO_2 corrosion has gained a very serious concern with the use of enhanced oil recovery techniques based on CO_2 injection reservoirs and sweet gas production from deeper wells [5–7].

The addition of corrosion inhibitors is a standard practice in oil and gas production systems to control the corrosion of carbon steel structures. The choice of the inhibitor is based on two considerations: first it could be synthesized conveniently from relatively cheap raw materials, secondly, it contains the electron cloud on the aromatic ring or, the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds [8]. Surfactant inhibitors have been successfully used in these applications [9, 10]. The corrosion inhibition of organic compounds is related to their adsorption properties. Adsorption depends on the nature and state of the metal surface, on the type of corrosive environment, and on the chemical structure of the inhibitor [11].

In the present work, the inhibition efficiency of the sulfated fatty acid amides surfactants for carbon steel in CO₂-saturated 1% NaCl solution was evaluated using Tafel polarization and linear polarization resistance corrosion rate measurements. In addition, the adsorption isotherm of the surfactants was investigated.

2. Experimental procedure

2.1. Chemical composition of carbon steel alloy

Electrodes are made up of carbon steel grade 080A15 and have a surface area of 4.55 cm^2 . The mechanical properties of the carbon steel measured at room temperature were provided by supplier shown as follows: tensile strength equal to 490 MPa and elongation to failure equal to 16%. The Chemical composition of

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low carbon steel used in this study was given in Table 1. The data was provided by European Corrosion Supplies Ltd.

Table 1: Chemical composition of low carbon steel alloy.

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

2.2. Synthesis of Surfactants

Sunflower oil was reacted with diethanolamine for 7 hours at 150-160 °C. These processes produce fatty acid diethanolamine amide. Based on the last prepared compound sulfating syntheses were performed. 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 , $-NH-CH_2-CH_2-O$, $-N-(CH_2-CH_2-OH)_2$ and $-N(CH_3)_2$). List of the synthesized surfactants are shown in Table 2.

2.3. Preparation of solutions

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 100 ppm used for corrosion measurements. All inhibitors solutions were prepared using a mixture from distilled water and alcohol in a different ratio.

Table 2: List of the synthesized surfactants includes, code number, name and structure.

Code number of the inhibitor	Name and abbreviation	Structure	molecular weight (g /mol)
I	Sodium salt of sulfated fatty acid diethanolamine amide (SS)	$\begin{array}{c} & & & \\ & & & \\ R-(CH_2)_8-CH-(CH_2)_7-C-N \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & $	449
п	Potassium salt of sulfated fatty acid diethanolamine amide (PS)	$\begin{array}{c c} & & & & \\ & & & \\ R-(CH_2)_8^- CH-(CH_2)_7 C-N & CH_2-CH_2-OH \\ & & & \\ & & & \\ O & & & \\ & & & \\ O & & \\ O$	465
ш	Ammonium salt of sulfated fatty acid diethanolamine amide (AS)	$\begin{array}{c} 0\\ H\\ R\cdot(CH_2)_{\delta} \cdot CH_2(CH_2)_{T} C\cdot N \leftarrow CH_2 \cdot CH_2 \cdot OH\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$	443
IV	Sulfated fatty acid diethanolamine amide- monoethanolamine complex (MC)	$\begin{array}{c} 0 \\ R \ (CH_2)_{3^-} \ CH \ (CH_2)_{7^-} C \ N \ CH_2 \ CH_2 \ OH \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	475
v	Sulfated fatty acid diethanolamine amide- diethanolamine Complex (DC)	$\begin{array}{c} & & & \\ & & \\ R_{-}(CH_2)_{3^-}CH_{+}(CH_2)_{7^-}C.N_{-}CH_2-CH_2-OH \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ $	524
VI	Sulfated fatty acid diethanolamine amide- dimethylamine Complex (DM)	$\begin{array}{c} 0 \\ R-(CH_2)_8-CH-(CH_2)_7-C-N \\ O \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	476

2.4. Corrosion measurements

The measurements were performed on the rotating cylinder electrode. This electrode was used for one time. The reference electrode was Ag/AgCl electrode to which all potentials are referred.

Before beginning the experiment, the prepared 1% - of sodium chloride solution was stirred by a magnetic stirrer for 60 min in

1000 ml cell. Then this cell was thermostated at a temperature 50 ° C for 1 hour under a pressure of 0.9 bars. The solution was saturated with carbon dioxide. To remove any surface contamination and air formed oxide, the working electrode was kept at–1500 mV (Ag/AgCl) for 5 min in the tested solution, disconnected shaken free of adsorbed hydrogen bubbles and then cathodic and anodic polarization was recorded. ACM Gill

AC instrument connected with a personal computer was used for the measurements.

2.4.1. The extrapolation of cathodic and anodic Tafel lines

The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range ± 100 mV with respect to corrosion potential (E_{corr}) at scan rate of 1 mV/s.

2.4.2. Linear polarization resistance 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. The prepared 1% - of the solution sodium chloride was stirred by a magnetic stirrer for 60 min in 4000 ml. The prepared solution poured into the 4 glass beakers (1000 ml for each one). Then these beakers were placed on a heater at 50 ° C for 1 hour under a pressure of 0.9 bars. The solution was saturated with carbon dioxide. After that, the electrodes were placed in the medium and are connected through a potentiometer ACM GILL AC. The surface of working electrode is cleaned by acetone before using, these electrodes are using for one time. After 1 hour, except for 1 beaker, the remaining 3 is fed with the suitable amount of inhibitor and continued supply of CO₂ under pressure of 0.9 bar until the end of the experiment.

The potential of the working electrode was varied by a CoreRunning programme (Version 5.1.3.) through an ACM instrument Gill AC. The CoreRunning programme converts a corrosion current in mA/cm² to a corrosion rate in mm/year. A cylindrical carbon steel rod of the composition 080A15 GRADE STEEL was used as a working electrode. Gill AC technology allows measure DC and AC signals using standard Sequencer software. A small sweep from typically -10 mV to +10 mV at 10 mV/min around the rest potential is performed. The test conditions are summarized in Table 3.

2.5. Surface characterization

In order to observe any changes in surface morphologies of the carbon steel samples after testing, the specimens were first immersed in the test media with and without an inhibitor for 5 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.

2.6. Methods of evaluation of corrosion parameters

Steady state of open circuit corrosion potential ($E_{\rm corr}$) for the investigated electrode in the absence and presence of the studied inhibitor was attained after 50–60 min from the moment of immersion. Corrosion current density ($I_{\rm corr}$) of the investigated electrodes was determined [12], by extrapolation of cathodic and anodic Tafel lines to corrosion potential ($E_{\rm corr}$). The inhibition efficiency expressed as percent inhibition (η %) is defined as:

$$\eta\% = \frac{I_{uninh.} - I_{inh.}}{I_{uninh.}} \times 100 \tag{1}$$

where $I_{\text{uninh.}}$ and $I_{\text{inh.}}$ are the uninhibited and inhibited corrosion currents. The inhibited corrosion currents are those determined in the presence of the studied surfactants used in this investigation. The uninhibited corrosion currents were determined in pure (inhibitor free) CO₂-saturated 1% NaCl solution at the same temperature.

Table 3: Test parameters for corrosion experiments.

Material	C1018 carbon steel			
RCE outer surface	4.55			
area/cm ²				
Solution volume/L	1.0			
Temperature/ °C	50			
pH	6.78 →5.70			
Inhibitor concentration,	25, 50, 75 and 100			
ppm				
pCO ₂ /bar	0.90			
NaCl concentration/wt%	1.0			
CO ₂ quality	> 99.7%			
Solution stirring	Stirred			
Corrosion measurements	 Linear Polarisation Resistance 			
	corrosion rate			
	The extrapolation of cathodic			
	and anodic Tafel lines.			

3. Results and discussions 3.1. 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_2 at a temperature equivalent to that in the field. During the test, CO_2 gas is purged 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.

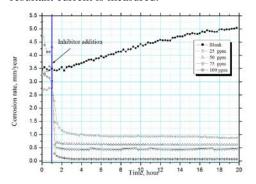


Figure 1 Variation of the Corrosion rate with time for carbon steel in CO_2 -saturated brine containing different concentrations of inhibitor I at 50 °C.

Figures 1 shows that, the change in corrosion rate (CR) with time for carbon steel in CO_2 -saturated 1%NaCl solution containing different concentrations form inhibitor I at 50 °C (as examples). The inhibitor was added after 1 hour of exposure because at this time the corrosion potential got stable, allowing the measurement of the CR prior the injection of the

inhibitor. The initial corrosion rate, without inhibitor, was measured to be between 3.45 and 5.03 mm y⁻¹. It can be observed from Figure 1 that the CR, in the absence of inhibitor, tends to increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite (Fe₃C) which is a part of the original steel in the non-oxidized state and accumulates on the surface after the preferential dissolution of ferrite (α -Fe) into Fe²⁺ [13]. Fe₃C is known to be less active than the ferrite phase. Therefore, there is a preferential dissolution of ferrite over cementite, working the former as the anode and latter as the cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process [13, 14].

Variation of the corrosion rate for inhibitor I at different concentrations is presented in Figure 1. Corrosion parameters were calculated on the basis of LPR corrosion rate test. The inhibition efficiency (η %) and surface coverage (θ) were calculated according to the following equations [9]:

$$\eta\% = \frac{CR_0 - CR_i}{CR_0} \times 100 \tag{2}$$

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

where CR_{\circ} is the corrosion rate without inhibitor and CR_{i} is 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 surfactants, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 91.9 and 98.7 % at 100 ppm after 20 hour of exposure (Figure 2). This trend may results from the fact that adsorption and surface coverage increase with the increase in concentration; thus the surface is effectively separated from the medium [15].

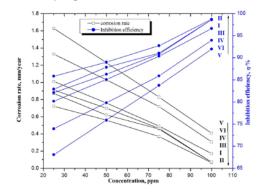


Figure 2 Dependence of inhibition efficiency and corrosion rate of carbon steel on the concentrations of inhibitors in CO_2 -saturated brine at 50 °C.

Figure 2 shows the values of corrosion rates and the inhibition efficiencies in the presence of different concentrations of different inhibitors at 50 °C. The data exhibited that, the corrosion rates and the inhibition are found to depend on the concentrations of the inhibitors. The corrosion rate (CR) are decreased, and the inhibition efficiencies (η %) and are increased with the increase of the surfactant concentrations. This indicates that the inhibitory action of the inhibitors

against carbon steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limits the dissolution of carbon steel, and the adsorption amounts of surfactants on carbon steel increase with concentrations in the corrosive solutions.

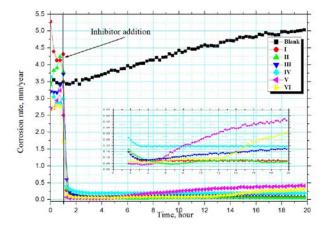


Figure 3 Variation of the corrosion rate with time for carbon steel in CO_2 -saturated brine containing 100 ppm from different inhibitors at 50 °C.

Figure 3 shows the variation of the corrosion rate with time for carbon steel in CO2-saturated 1% NaCl solution containing 100 ppm from different sulfated fatty acid amides surfactants at 50 °C. This plot indicates that, the presence of all surfactants decreases the rate of corrosion. However, the maximum decrease in the corrosion rate was observed for inhibitor (II) and the inhibition efficiency of the investigated surfactants was increased in the following order: II> I> III> IV > VI >V. There was an increase in the efficiency of corrosion inhibition with increasing concentration, Due to their containment of C=O, oxygen, nitrogen and sulfur groups these molecules contribute towards inhibition, and effectively protecting the surface. Adsorption of these surface active molecules 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 active inhibitor molecules, any synergetic effects with other molecules present in the environment and/or flow/shear effects.

The high inhibition efficiency obtained in CO_2 - saturated 1% NaCl solution in the presence of studied inhibitors can be attributed to the formation of a protective film of iron carbonate (FeCO₃) as follows [16]:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)}$$
(4)

$$(5)$$

$$H_2CO_{3(aq)} \leftrightarrow H^+ + HCO_3^-$$
(6)

$$HCO_{3}^{-} \leftrightarrow \mathrm{H}^{+} + CO_{3}^{2-} \tag{7}$$

The anodic dissolution for iron in carbonic acid solutions gives ferrous ions [16].

$$Fe \leftrightarrow Fe^{2+} + 2e^{-}$$
 (8)

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_2 environments. Ogundele and White suggested that, iron carbonate, FeCO₃, may be important in the formation of protective layers on steel surface [17]. The formation of iron carbonate can be explained by using the following Eq.[18]. Fe²⁺ + $CO_3^{2-} \rightarrow$ FeCO₃ (9)

3.2. Extrapolation of cathodic and anodic Tafel lines

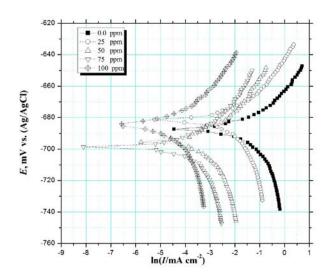


Figure 4 Tafel polarization curves for carbon steel in CO_2 -saturated brine containing different concentration of inhibitor (I) at 50 °C.

Figure 4 shows the influence of inhibitor I concentrations on the Tafel cathodic and anodic polarization characteristics of carbon steel in CO2-saturated brine at scan rate 1 mV/s and at 50 °C. Corrosion parameters were calculated on the basis of cathodic and anodic potential versus current density characteristics in the Tafel potential region [19, 20]. 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}) . It can be seen that the presence of surfactants molecule results a marked shift in both cathodic and anodic branches of the polarization curves towards lower current densities. This means that, the inhibitors affect both cathodic and anodic reactions. It was found that, both anodic and cathodic reactions of carbon steel electrode corrosion were inhibited with increasing concentration of synthesized inhibitors. These results suggest that not only the addition of synthesized inhibitors reduce anodic dissolution but also retard the hydrogen evolution reaction. The results showed that the inhibiting action of these inhibitors on both cathodic and anodic processes seems to approximately be equal. The inhibitor may decrease the corrosion through the reduction of carbon steel reactivity. Accordingly to this mechanism, a reduction of either the anodic or the cathodic reaction or both

arises from the adsorption of the inhibitor on the corresponding active sites [21].

Table 4: Corrosion parameters obtained from Tafel polarization for carbon steel in CO_2 -saturted 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>E</i> _{corr} (mV (Ag/AgCl))	(mAcm ⁻²)	β _a (mVdec ⁻¹)	-βε (mVdec ⁻¹)	θ	1 %
Absence	0.0	687	0.389	44	107	20 -	
	25	680	0.070	43	99	0.82	82
	50	695	0.051	36	100	0.86	86.
I	75	698	0.039	38	105	0.89	89.9
200	684	0.010	40	103	0.97	97.	
	25	686	0.059	39	102	0.84	84.
п	50	692	0.047	39	98	0.87	87.9
	75	688	0.032	42	101	0.91	91.
	100	695	0.009	38	106	0.97	97
ш	25	695	0.073	39	103	0.81	81.
	50	690	0.057	44	101	0.85	85
	75	687	0.040	39	100	0.89	89:
	100	689	0.010	37	98	0.97	97
	25	694	0.081	45	99	0.79	79.
	50	687	0.062	42	105	0.84	84
IV	75	688	0.042	40	103	0.89	89
	100	691	0.017	37	102	0.95	95
v	25	693	0.128	36	99	0.67	67.
	50	695	0.098	38	96	0.74	743
	75	687	0.067	40	99	0.82	82.
	100	699	0.035	42	97	0.91	91
VI	25	686	0.105	42	100	0.73	73
	50	701	0.082	41	98	0.78	78.
	75	704	0.059	38	99	0.84	843
	100	690	0.028	35	105	0.92	92

The electrochemical parameters E_{corr} , I_{corr} , inhibition efficiency $(\eta\%)$, anodic and cathodic Tafel slopes (β_a, β_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 electrodes processes occurs, at both cathodic and anodic sites, as a result of coverage of these sites by surfactants molecules. However, the maximum decrease in $I_{\rm corr}$ was observed for (II). This may be attributed to the increase of the electron densities and the molecular size [22, 23]. 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 [24]. The E_{corr} values of all synthesized inhibitors were shifted slightly toward both cathodic and anodic directions and did not show any definite trend in CO₂-saturated brine. This may be considered due to the mixed-type behaviour of the studied surfactants. It can be observed, the shift in $E_{\rm corr}$ that is characteristic of anodic and anodic/cathodic inhibitor [25]. It was explained that this shift in $E_{\rm corr}$ is due to active sites blocking effect that occurs when an inhibitor is added [26]. In the case of CO₂ corrosion the anodic and cathodic reactions are the oxidation of iron and the reduction of hydrogen, respectively [27]. If it is considered that the active sites on the metal surface are the same for both reactions before adding the inhibitor, it is logical the change in $E_{\rm corr}$ when the inhibitor is present because its adsorption change those active sites and therefore the anodic and cathodic reaction rates [28].

The fact that the slopes of the cathodic (β_c) and anodic (β_a) Tafel lines in Table 4 are approximately constant and independent of inhibitor concentration. These results indicate that this inhibitors act by simply blocking the available surface area. In other words, the inhibitor decreases the surface area for corrosion of the investigated metal, and only causes inactivation of a part of the surface with respect to corrosive medium [24]. On the other hand, the cathodic Tafel slopes (β_c) are also found to be greater than the respective anodic Tafel slopes (β_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 CO₂ saturated solution are under cathodic control.

Data in Table 4 shows that the inhibition efficiency increased with increasing the inhibitor concentrations. The inhibition efficiency of the investigated surfactants was increased in the following order: II> I> III> IV > VI >V. Conclusively, the surfactant inhibitor, having near unity θ (see Table 4), was considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of carbon steel significantly. The inhibition efficiencies are in a good agreement with that calculated from LPR corrosion rate measurements.

3.3. Adsorption isotherm

Classical adsorption isotherms have been used extensively in the study of adsorption of organic substances onto steel electrodes. It is widely acknowledged that they provide useful insights into the mechanism of corrosion inhibition [29]. A determination of the type of adsorption isotherm itself provides information on the adsorption process such as surface coverage, adsorption equilibrium constant and information on the interaction between the organic compound and electrode surface [30].

The interaction between the inhibitors and carbon steel surface can be described by the adsorption isotherm. During corrosion inhibition of metals, the nature of the inhibitor on the corroding surface has been deduced in terms of adsorption characteristics of the inhibitor. Furthermore, the solvent (H₂O) molecules could also be adsorbed at metal/solution interface. So the adsorption of surfactants molecules from aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [Surfactant_(sol.)] and water molecules at the electrode surface [H₂O_(ads)] [30]:

Surfactant $_{(sol.)} + xH_2O_{(ads.)} = Surfactant _{(ads.)} + xH_2O_{(sol.)}$ (10)

where x is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. Basic information on the interaction between the inhibitor and the carbon steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between the degree of surface coverage (θ) and inhibitor concentration (C) must be found. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm. The Langmuir isotherm is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites, whether occupied or not [31]. According to this isotherm, θ is related to C by:

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

where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C_{inh} is the surfactant concentration.

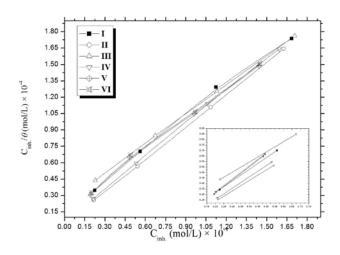


Figure 5 Curve fitting of the corrosion data obtained from LPR corrosion rate measurements for carbon steel in CO_2 saturated brine containing various concentrations of inhibitors according to Langmuir adsorption isotherm model at 50 °C.

Figure 5 shows the plots of C/θ against inhibitor concentrations (C) at 323K and the expected linear relationship is obtained for all investigated surfactants with excellent correlation coefficients (R^2) (Table 5), confirming the validity of this approach. The slopes of the straight lines are unity, suggesting that adsorbed surfactant molecules form monolayer on the carbon steel surface and there is no interaction among the adsorbed inhibitor molecules.

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 (ΔG_{ads}^o) calculated from [30]:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right) \tag{12}$$

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 [32].

The high values of K_{ads} for the studied surfactants indicate stronger adsorption on the metal steel surface in CO₂-saturated brine. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency [33]. The large value of K_{ads} obtained for the studied surfactants agree with the high inhibition efficiency obtained.

Generally, values of ΔG_{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 [34]. In the present study, The values of ΔG_{ads}^{o} obtained for studied surfactants on carbon steel in CO₂-saturated solution ranges between -41.61 and -42.4 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 CO₂ 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 sp² electron pairs present on the N, S and/or O atoms of the inhibitor. The high and negative values obtained for ΔG_{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} .

Table 5: Thermodynamic parameters for the adsorption of the

Inhibitors Code	Slope	Regression coefficients, <i>R</i> ²	$K_{\rm ads},$ M ⁻¹	ΔG^o_{ads} (kJ mol ⁻¹)
Ι	1.03	0.9876	12.65×10 ⁴	-42.26
II	1.08	0.9893	13.16×10^{4}	-42.40
III	1.03	0.9512	11.79×10^{4}	-42.10
IV	1.02	0.9773	10.82×10^{4}	-41.87
\mathbf{V}	1.01	0.9862	9.84×10^{4}	-41.61
VI	1.01	0.9862	10.24×10^{4}	-41.72

studied surfactants on carbon steel electrode in CO_2 - saturated 1% NaCl solution.

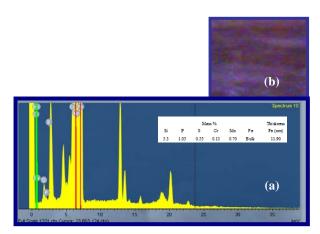


Figure 6 EDRF analysis of carbon steel electrode surface after immersion in CO_2 -saturated solution for 5 days without inhibitor (a) and the picture at the same conditions (b).

3.4. Surface characterization

Figures 6a and 7a show an EDRF spectroscopy for the carbon steel surface after immersed in CO_2 -saturated 1% NaCl solution without and with 100 ppm of inhibitor I for 5 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. However, the data in Fig. 7a in the presence of 100 ppm of inhibitor I show additional peak characteristic of Na 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.

Figures 6b, 7b show the picture of the passive film formed on the carbon steel surface after immersion in CO_2 -saturated brine for 5 days in the absence and presence of inhibitor **I**. In the absence of inhibitor (Fig. 6b), 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. 7b shows the image of the electrode surface in presence of 100 ppm of the investigated inhibitor. The image reveal that, the surface is almost free from damages and it is smooth, which indicates a good protective film present on the carbon steel surface and also confirms the highest inhibition efficiency of the prepared complex surfactants.

From quantitative analysis (Fig. 6, 7 b), it can be observed that, there is a decrease in the mass thickness of iron on the electrode surface after corrosion process in corrosive media without inhibitors, but in the presence of 100 ppm of inhibitor **I**, the mass thickness increased to 13.35 mm. This indicates that, the presence of inhibitor in CO_2 - saturated brine an adsorbed layer is formed on the electrode surface, which successfully inhibits corrosion processes.

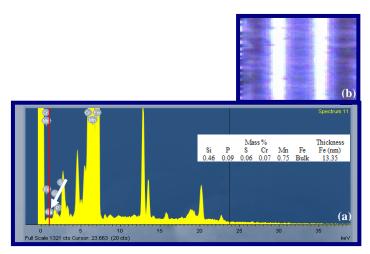


Figure 7 EDRF analysis of carbon steel electrode surface after immersion in CO_2 -saturated solution containing 100 ppm inhibitor I for 5 days (a) and the picture at the same conditions (b).

4. Conclusions

LPR corrosion rate and extrapolation of cathodic and anodic Tafel lines methods were employed to study the corrosion inhibition of carbon steel in CO₂-saturated 1% NaCl solution using some sulfated Fatty acid amide surfactants based on sunflower oil as corrosion inhibitors. The principal conclusions are: 1. All studied sulfated Fatty acid amide surfactants were found to be effective inhibitors for carbon steel corrosion in CO₂-saturated solutions.

2. The data obtained from the two methods used are in a good agreement with each other. The inhibition efficiency increased as concentration of the inhibitor is increased, getting maximum inhibition efficiency ranged between 91.9 and 98.7 % at 100 ppm.

3. The corrosion process is inhibited by the adsorption of these surfactants on carbon steel surface. Inhibition efficiency was found to be in the following order: II> I > III>IV>V>VI.

4. The adsorption of synthesized surfactants on carbon steel surface obeyed Langmuir adsorption isotherm. The values of the free energy for the adsorption process indicate that, the studied surfactants are chemically adsorbed on the metal surface.

5.EDRF observations of the electrode surface showed that a good protective film present on the metal surface and also confirms the highest inhibition efficiency of the prepared sulfated Fatty acid amides surfactants.

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