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Carbon Dioxide Corrosion Inhibition of Carbon Steel by using some surfactants based on sunflower oil and monoethanlamine

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ABSTRACT

Novel surfactants based on sunflower oil and monoethanlamine were tested as inhibitors for the corrosion of steel in CO_2 -saturated 1% NaCl solution by Potentiodynamic polarization measurements and linear polarization resistance corrosion rate (LPR bubble test) at 50 °C. Inhibition efficiency increased with increase in the concentration of the studied compounds. Results show that the order of inhibition efficiency is II> II > IV >V. The adsorption of the inhibitors on the steel surface obeys Langmuir model and was physisorption.

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Keywords

Sunflower oil, Monoethanlamine, Surfactants, Carbon steel, CO₂-saturated solution.

Introduction

Corrosion of materials has continued to receive interest in the technological world. In the field of corrosion inhibition, scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. Addition of corrosion inhibitors to the corrosion environment with respect to the other methods of corrosion inhibition has been employed [1]. Corrosion inhibition of materials has been the focus of research for centuries and in many cases has been well analyzed and understood [2- 4].

In that sense, use of surfactants as inhibitors is one of the best-known methods of corrosion protection [5-8]. Surfactants, when used as inhibitors, act through a process of surface adsorption. Adsorption of surfactant on solid surfaces can modify the surface charge, and also the hydrophobic and other key properties of the solid surface that influence interfacial processes. In general adsorption is governed by different types of forces, such as covalent bonding, electrostatic attraction, hydrogen bonding, etc. [9]. The adsorption of the surfactant on the metal surface can markedly change the corrosion-resisting property of the metal [8], and so the study of the relationship between the adsorption and corrosion inhibition is of great importance.

In the present work, we describe the synthesis of a novel surfactants based on sunflower oil and monoethanlamine. Corrosion inhibition of carbon steel in CO₂-saturated 1% NaCl solution in the presence of instigated surfactants studied by using Potentiodynamic polarization measurements and linear polarization resistance corrosion rate (LPR bubble test) at 50 °C, and possible adsorption mechanism of the surfactants on the metal surface in the corrosive media is also described.

Materials and methods

Chemical composition of carbon steel alloy

Electrodes are made of carbon steel grade 080A15 and have an area of 4.55 cm^2 . The Chemical composition of low carbon

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

Table	1: Che	mical	compo	osition	of low	carbo	n 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

Synthesis of Surfactants

Sunflower oil was reacted with monoethanolamine for 14 hours at 150-160 °C. These processes produce fatty acid monoethanolamine amide. Based on the last prepared compound sulfating syntheses were performed. The product is sulfated fatty acid monoethanolamine amide. Five types from surfactants were synthesized in high purity by the following composition: [*R*-*CH*-(*OSO*₃*M*)-*CONH*-*CH*₂-*CH*₂-*OH*] (where M = Na, *K*, *NH*₄, -*NH*-*CH*₂-*CH*₂-*OH* and -*N*-(*CH*₂-*CH*₂-*OH*)₂). List of the synthesized surfactants are shown in Table **2**. The chemical structure of the synthesized surfactants was characterized by using FT-IR, Spectrum BX spectrometer using KBr disks.

Preparation of solutions The aggressive solution.

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.

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 NaCl 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

19830

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.

Potentiodynamic polarization measurements

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.

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 CO_2 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.

Results and discussion

Chemical structure of the synthesized surfactants

The structural characteristic of fatty acid monoethanolamine amide before and after sulfating processes was confirmed by FT-IR spectroscopy in the range 4000–500 cm⁻¹. The peak at about 1740 cm⁻¹ is duo to the –NH-C=O carbonyl group, whereas the peak at 1459 cm⁻¹ arises due to C=C bond. This bond was broken after sulfating process. The peak at 1377 cm⁻¹ is due to S-O stretching absorption bands. FTIR spectrum showed that, the presence of OH group after sulfating process. It indicates the almost complete removal of C=C bond by sulfating process and the process occur only on C=C.

Linear polarization studies (LPR bubble test)

Linear polarization studies were made using a "LPR bubble test" method. 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.

LPR test has been performed in brine saturated with CO₂ at 50 °C, in turbulence fluid stream during 20 hours. Figure **1** shows that, the change in corrosion rate (CR) with time for carbon steel in CO₂-saturated 1%NaCl solution containing different concentrations form inhibitors (a) **I**, (b) **II** and (c) **V** 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 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, but in the presence 100 ppm of the investigated inhibitors between 1.496 and 0.047 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⁺ [10]. 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 [11, 12]. Corrosion parameters were calculated on the basis of LPR test. It can be seen that the presence of inhibitors results a high decrease in the rate of corrosion. This may be contributed to stable protective film which formed on the metal surface [13]. The data in Table 3 exhibited that the corrosion rate decreases, and the inhibition efficiency (IE %) increases as the concentration of inhibitors is increased. 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 [14].

Figure 2 shows the Effect of different surfactants (100 ppm) on the kinetics corrosion of carbon steel in 1% NaCl solution saturated with CO₂ 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 (II) and the inhibition efficiency of the investigated inhibitors was increased in the following order: II> I> III > IV >V (after 20 hours). Higher molecular size and high electron density on the adsorption centers may be responsible for high corrosion efficiency [15].

The high inhibition efficiency obtained in CO_2 - 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 (FeCO₃) as follows [16]:

 $CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{1}$

 $CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)}$ (2) $H_2CO_{3(aq)} \leftrightarrow H^+ + HCO_2^-$ (3)

 $11CO_3$

$$HCO_{3}^{-} \leftrightarrow \mathrm{H}^{+} + CO_{3}^{2-} \tag{4}$$

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

$$Fe \leftrightarrow Fe^{2+} + 2e^{-}$$
 (5)

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 CO₂ 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]. $Fe^{2+} + CO^{2-} \rightarrow FeCO_3$ (5)





Figure 1: Variation of the Corrosion rate with time for carbon steel in CO₂-saturated 1 % NaCl solution containing different concentrations of inhibitors (a) I, (b) II and (c) V based on sunflower oil at 50 °C.



Figure 2: Variation of the Corrosion rate with time for carbon steel in CO₂-saturated 1% NaCl solution containing 100 ppm of different inhibitors at 50 °C

Potentiodynamic polarization measurements

Figure 1 shows the influence of inhibitor II concentrations on the Tafel cathodic and anodic polarization characteristics of mild steel in CO₂-saturated solution 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]. Steady state of open circuit corrosion potential (E_{corr}) for the investigated electrode in the absence and presence of the studied inhibitor was attained after 45–60 min from the moment of immersion. Corrosion current density (I_{corr}) of the investigated electrodes was determined [21], by extrapolation of cathodic and anodic Tafel lines to corrosion potential (E_{corr}). The inhibition efficiency expressed as percent inhibition (IE%) is defined as:

$$IE\% = \frac{I_{uninh} - I_{inh.}}{I_{uninh}} \times 100$$
⁽⁶⁾

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. 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 mild 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 electrochemical parameters E_{corr} , I_{corr} , inhibition efficiency (*IE*%), anodic and cathodic Tafel slopes (β_a , β_c) obtained from the polarization measurements were listed in Table 2. The data exhibited that, the corrosion current density (I_{corr}) decreases, and the inhibition efficiency (IE%) 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) and the inhibition efficiency of the investigated inhibitors was increased in the following order: II> I > III > IV > V at 100 ppm. 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 [22, 23]. The $E_{\rm corr}$ 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 behavior of the studied inhibitors. It can be observed, the shift in $E_{\rm corr}$ that is characteristic of anodic and anodic/cathodic inhibitor [24].

The change in β_a and β_c values as shown in Table 2 indicates that adsorption of synthesized surfactants modify the mechanism of anodic dissolution as well as cathodic hydrogen evolution. 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 [23]. 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 cathodic exchange-current density values are less than those of the anodic counter parts. It can be concluded that the overall kinetics of corrosion of mild steel alloy in CO₂ saturated solution are under cathodic control.

Adsorption isotherm

In order to obtain the isotherm, the linear relation between θ values and C_{inh} 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 is obtained with the Langmuir isotherm. This model has also been used for other inhibitor systems [25, 26]. According to this isotherm, θ is related to C_{inh} by [27]:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}}$$
(7)

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

Code number of the inhibitor	Name and abbreviation	Structure	molecular weight (g /mol)				
I	Sodium salt of sulfated fatty acid monoethanolamine amide (SS)	$ \begin{array}{c} & O \\ I \\ R-(CH_2)_8-CH-(CH_2)_7-C-NH-CH_2-CH_2-OH \\ & O \\ & O \\ O$	401				
п	Potassium salt of sulfated fatty acid monoethanolamine amide (PS)	$ \begin{array}{c} & & \\ & & \\ & & \\ R-(CH_2)_8-CH-(CH_2)_7-C-NH-CH_2-CH_2-OH \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$	417				
ш	Ammonium salt of sulfated fatty acid monoethanolamine amide (AS)	$ \begin{array}{c} & & \\ & & \\ & & \\ R-(CH_2)_8-CH-(CH_2)_7-C-NH-CH_2-CH_2-OH \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$	395				
IV	Sulfated fatty acid monoethanolamine amide - monoethanolamine complex (MC)	$\begin{array}{c} & & & \\ & & & \\ R-(CH_2)_8-CH-(CH_2)_7-C-NH-CH_2-CH_2-OH \\ & & & \\ O & & \\ & & O \\ & & & \\ O & & \\ & & & O \\ & & \\ O & & \\ \end{array}$	427				
V	Sulfated fatty acid monoethanolamine amide - diethanolamine Complex (DC)	$ \begin{array}{c} & & \\ & & \\ R-(CH_2)_{8^-}CH-(CH_2)_{7^-}C-NH-CH_2-CH_2-OH \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ O \end{array} \\ \begin{array}{c} & \\ & O \end{array} \\ & & \\ & & \\ O \end{array} \\ \begin{array}{c} O \\ & \\ & \\ O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ & & \\ & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ \\ & & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ \\ & & O \end{array} \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ \\ & & O \end{array} \\ \\ \begin{array}{c} O \\ & \\ & O \end{array} \\ \\ \\ & O \end{array} \\ \\ \end{array} $	476				

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

Table 3: The corrosion parameters obtained from LPR corrosion rate measurements for mild steel electrode in CO_2 saturated 1% solution of NaCl in the absence and presence of various concentrations of inhibitors obtained based on sunflower oil at 50 ° C

Inhibitors	Concentration, ppm	Corrosion rate (mm/year)	Surface coverage θ	The inhibition efficiency, <i>IE</i> %
Absence	0.0	5.0373		
T	25	0.155	0.96	96.92
1	50	0.0617	0.98	98.77
п	25	0.076	0.98	98.49
11	50	0.047	0.99	99.06
ш	25	0.321	0.93	93.62
111	50	0.041	0.99	98.18
IV	25	0.424	0.91	91.58
IV	50	0.288	0.94	94.28
V	25	1.496	0.70	70.30
v	50	0.720	0.85	85.70

 Table 4: Corrosion parameters obtained from Tafel polarization for carbon steel in CO2-saturted 1% NaCl solution in the absence and presence of different concentrations of the prepared surfactants at 50 °C

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Inhibitors Code	Conc. of inhibitor (ppm)	-E _{corr} (mV (Ag/AgCl))	I _{corr} (mAcm ⁻²)	$ \begin{array}{c} \beta_{a} \\ (mVdec^{-1}) \end{array} $	-β _c (mVdec ⁻¹)	θ	IE%
Absence	0.0	687	0.389	44	107		
	25	618	0.050	41	97	0.8702	87.02
т	50	631	0.013	34	98	0.9651	96.51
1	75	634	0.011	36	103	0.9710	97.1
	100	621	0.006	38	101	0.9836	98.36
	25	623	0.029	37	100	0.9246	92.46
п	50	629	0.007	37	96	0.9808	98.08
11	75	625	0.005	40	99	0.9858	98.58
	100	631	0.005	36	104	0.9865	98.65
	25	631	0.051	37	101	0.8679	86.79
ш	50	627	0.026	42	99	0.9321	93.21
111	75	624	0.018	37	98	0.9529	95.29
	100	626	0.004	35	96	0.9877	98.77
	25	630	0.071	43	97	0.8169	81.69
IV/	50	624	0.034	40	103	0.9117	91.17
1 V	75	625	0.043	38	101	0.8879	88.79
	100	628	0.023	35	100	0.9387	93.87
	25	630	0.129	34	97	0.6669	66.69
V	50	631	0.117	36	94	0.6989	69.89
v	75	624	0.068	38	97	0.8229	82.29
	100	635	0.057	40	95	0.8529	85.29

Plots of C_{inh}/θ versus C_{inh} yielded a straight line as shown in Fig.4, which suggested that the adsorption of inhibitors on metal surface obeyed Langmuir adsorption isotherm model. This isotherm assumed that the adsorbed molecules occupied only one site and there was no interaction with other molecules adsorbed. The linear regression coefficients (\mathbb{R}^2) and the slopes parameter variations were calculated. All correlation coefficient ($\mathbb{R}^2 > 0.9799$) indicated that the inhibition of carbon steel by these inhibitors was attributed to the adsorption of surfactant molecule on the metal surface. However, the slopes of the C_{inh}/θ versus C_{inh} plots were close to 1 and showed a little deviation from unity which meant non-ideal simulating [28] and unexpected from Langmuir adsorption isotherm. They might be the results of the interactions between the adsorbed species on the metal surface [29, 30].



Figure 3: Polarization plots of carbon steel electrode obtained in CO₂-saturated 1% NaCl solution containing different concentration of inhibitor (II) at 50 °C

The values of *K* obtained from the Langmuir adsorption isotherm are calculated, together with the values of the Gibbs free energy of adsorption (ΔG^o_{ads}) calculated from

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right)^{ads}$$
(8)

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

The high value of the adsorption-desorption equilibrium constant as represented in Fig.4, reflects the high adsorption ability of this inhibitor on the carbon steel surface [31].

In general, values of the free energy of adsorption ΔG_{ads}^o , up to

-20 kJ/mol seem to suggest electrostatic interaction between the charged molecules and the charged metal (physical adsorption), while those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type (chemisorption bonds) [14]. The decreasing value of ΔG_{ads}^o reflects the increasing adsorption. The calculated values of ΔG_{ads}^o for synthesized

surfactants ranged between -26.51 and -18.32 kJ/mol, indicating that the adsorption of the studied surfactants takes place through electrostatic interaction between the inhibitor molecule and the carbon steel surface so physicosorption was supposed. The negative values of ΔG_{ads}^o indicate a spontaneous adsorption of

the surfactants on the surface of investigated electrode [31]. The

 ΔG_{ads}^{o} for inhibitor II (-26.51kJ/mol) was less than other surfactants which indicate the stronger adsorption for inhibitor II more than other surfactants.



Figure 4: Curve fitting of the corrosion data obtained from Potentiodynamic polarization measurements for carbon steel in CO₂ saturated brine containing various concentrations of inhibitors according to Langmuir adsorption isotherm model at 50 °C

Conclusion

1)All the studied surfactants showed good inhibition properties for the corrosion of carbon steel in CO₂-saturated 1% NaCl solution, and the inhibition efficiency increased with increasing the concentration of the inhibitors. The inhibiting efficiencies of surfactants decreased in the order of II> I> III > IV >V.

2) The initial corrosion rate, without inhibitor, was measured to be between 3.45 and 5.03 mm y⁻¹, but in the presence 100 ppm of the investigated inhibitors between 1.496 and 0.047 mm y⁻¹.

3)Based on the electrochemical tests, all the surfactants acted as mixed-type inhibitors.

4)The inhibiting efficiencies determined by polarization measurements were in good agreement with that from linear polarization resistance corrosion rate (LPR bubble test).

5)The adsorption of surfactants on the carbon steel obeyed the Langmuir adsorption isotherm model.

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