

Preparation, Surface active properties, and Anticorrosion Application of some novel surfactants based on cottonseed oil and diethanolamine on carbon steel in CO₂ environments

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ABSTRACT

Novel surfactants were synthesized based on cottonseed oil and diethanolamine and the structures of these compounds were confirmed by FTIR spectroscopy. The surface and thermodynamic properties of these compounds have been investigated. The corrosion behavior of the synthesized surfactant corrosion inhibitors was evaluated by using potentiodynamic (Tafel) polarization curves, linear polarization resistance corrosion rate techniques. The experimental results showed that these inhibitors revealed a very good corrosion inhibition even at low concentrations. The protection efficiency increased with increasing inhibitor concentration, getting maximum values ranged between 87.37 and 97.91 % at 100 ppm after 20 hour of exposure. The adsorption process was found to obey the Langmuir adsorption isotherm.

Indexing terms/Keywords

Corrosion inhibitor; Carbon steel; Surfactants; Potentiodynamic polarization; Surface tension; Critical micelle concentration

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INTRODUCTION

Carbonic-acid corrosion (CO_2 -corrosion) is one of the most studied forms of corrosion in the oil and gas industry. Carbon Dioxide gas (CO_2) in oil/gas stream forms carbonic acid (H_2CO_3) when dissolved in water (which is also contained in gas/crude oil reservoir/well) forms Carbonic acid (H_2CO_3) with the characteristic that it is more aggressive than hydrochloric acid at the same pH [1].

Mild steel is widely applied as the constructional material in many industries due to its excellent mechanical properties and low cost. As some of the important fields of application are acid pickling, industrial cleaning, acid descaling, oil-well acidizing and petrochemical processes, the main problem of applying mild steel is its dissolution in chloride solutions. Chloride is well known to play a crucial role in steel corrosion, but its effect depends on whether the aqueous system is deaerated (oxygen-free), oxygen-aerated, or deaerated but CO_2 -bearing. In deaerated acidic solutions, chloride accelerates the anodic kinetics of iron dissolution via a catalytic mechanism [2–5]. In deaerated neutral and alkaline solutions, a corrosion scale is usually formed.

Several methods are present for corrosion prevention. One of such methods is the use of organic inhibitors [6–11]. The use of inhibitors is the most economical and practical method in reducing corrosive attack on metals [12, 13]. Surfactant corrosion inhibitors are the most effective means of protection to sever corrosion of carbon steel constructions in the petroleum industry. The adsorption of a surfactant on a metal surface can markedly change the corrosion-resistance properties of the metal [14, 15]. Therefore, the study of the relation between the adsorption and corrosion inhibition is of great importance. Recently, many surfactants have been widely used as corrosion inhibitors for mild steel alloys in CO_2 environments [16, 17]. The compounds act through a process of surface adsorption. The efficiency of inhibitors depends on the nature of the metal surface and electrochemical potential at the interface. The structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface also has an effect on the efficiency of inhibitors [18–20].

The purpose of this paper is to evaluate the behavior of novel surfactants synthesized based on cottonseed oil and diethanolamine as corrosion inhibitors in the CO_2 corrosion of 1018 carbon steel using potentiodynamic (Tafel) polarization curves, linear polarization resistance corrosion rate techniques in an environment containing 1% NaCl solution and CO_2 . It was also the purpose of the present work to test the experimental data obtained from LPR corrosion rate measurements with several adsorption isotherms at the investigated temperature, in order to gain more information on the mode of adsorption.

EXPERIMENTAL PROCEDURE

Chemical composition of carbon steel alloy

Electrodes are made of carbon steel grade 080A15 and have an area of 4.55 cm². The mechanical properties of the carbon steel measured at room temperature were provided by the supplier shown as follows: tensile strength equal to 490 MPa and elongation to failure equal to 16%. 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: 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

Synthesis of Surfactants

Cottonseed 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 of surfactants were synthesized in high purity by the following compositions: $[\text{R}-\text{CH}(\text{OSO}_3\text{M})-\text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2]$ (where M = Na, K, NH_4 , $-\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ and $-\text{N}(\text{CH}_3)_2$). The chemical structure of the synthesized surfactants was characterized by using FT-IR, Spectrum BX spectrometer using KBr disks. List of the synthesized surfactants are shown in Table 2.

Preparation of solutions

The aggressive solution, 1% NaCl, was prepared by dissolving analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was from 25 to 100 ppm used for corrosion measurements. All inhibitor solutions were prepared using a mixture of 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 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.

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.

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.

Surface tension measurements

The surface tensions were determined by DuNouy Tensiometer, Kruss Type 8451 and the temperature was maintained precisely at 25 °C. Critical micelle concentration (CMC) values of surfactants were determined, according to the break points in plots of the surface tension versus ln molar concentration of investigated surfactants.

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)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{Na}^+$	445
II	Potassium salt of sulfated fatty acid diethanolamine amide (PS)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{K}^+$	461
III	Ammonium salt of sulfated fatty acid diethanolamine amide (AS)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{NH}_4^+$	439
IV	Sulfated fatty acid diethanolamine amide- monoethanolamine complex (MC)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{NH}_3^+ \text{CH}_2\text{CH}_2\text{OH}$	471
V	Sulfated fatty acid diethanolamine amide- diethanolamine Complex (DC)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{NH}_2 \cdot (\text{CH}_2\text{CH}_2\text{OH})_2$	520
VI	Sulfated fatty acid diethanolamine amide- dimethylamine Complex (DM)	$\text{R}-(\text{CH}_2)_8-\text{CH}(\text{CH}_2)_7-\text{C}-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \\ \parallel \\ \text{O} \end{array} \text{O}^- \text{NH}_2 \cdot (\text{CH}_3)_2$	472



Table 3: Test parameters for corrosion experiments.

Material	C1018 carbon steel
RCE outer surface area/cm ²	4.55
Solution volume/L	1.0
Temperature/ °C	50
pH	6.76 →5.68
Inhibitor concentration, ppm	25, 50, 75 and 100
pCO ₂ /bar	0.90
NaCl concentration/wt%	1.0
CO ₂ quality	> 99.7%
Solution stirring	Stirred
Corrosion measurements	<ul style="list-style-type: none">➤ Linear Polarization Resistance corrosion rate➤ The extrapolation of cathodic and anodic Tafel lines.

RESULTS AND DISCUSSIONS

Chemical structure of the synthesized surfactants

The structural characteristic of fatty acid diethanolamine amide before and after sulfating processes was confirmed by FT-IR spectroscopy in the range 4000–500 cm⁻¹. The peak at about 1690 cm⁻¹ is due to the –NH–C=O carbonyl group, whereas the peak at 1450 cm⁻¹ arises due to C=C bond. This bond was broken after sulfating process. The peak at 1350 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.

The FT-IR for compound V showed an absorption band at the 2325 cm⁻¹ region, indicating that formation ammonium ion (-⁺NH₂). In addition, there was a strong band at 890 cm⁻¹, indicating the presence of multiple (CH₂) groups. The very strong band at the 2850 region was due mainly to the methyl asymmetric stretching vibration. The sharp band at 2925 cm⁻¹ was observed for the investigated compounds due to the stretching vibration of the symmetric methylene group. The FT-IR absorption spectra confirmed that the disappearance of -OH band of –SO₂-OH (broad band), this confirmed the transfer of proton of acid to nitrogen atom of amine to form -⁺NH₂ group. The results are generally in agreement with the expected correlations.

Potentiodynamic (Tafel) polarization measurements

Figure 1 represents the anodic and cathodic potentiodynamic polarization curves of mild steel alloy in CO₂-saturated 1% NaCl solution in the absence and presence of different concentration of inhibitor I. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were obtained by the extrapolating anodic and cathodic Tafel lines of polarization curves [21, 22]. The results showed that a marked dependence of I_{corr} of mild steel alloy on the surfactant concentrations. The surfactant inhibit both cathodic and anodic parts of the polarization curves, the shape of the curves are not modified on adding the plant extracts or by increasing the concentration, but the more pronounced behaviour that the curves produces a little shift on the anodic region and a greater shift on the cathodic region.

The adsorbed inhibitor blocks either the anodic or cathodic reaction or both. The effect of the inhibitor may be due to changes in the electric double layer, by reducing metal reactivity, or by the inhibitor participation in partial electrode reaction and by formation of a physical barrier. The adsorbed inhibitor may not cover the entire metal surface, but occupies sites which are electrochemically active and thereby reduces the extent of anodic or cathodic reaction or both. The corrosion rate will be decreased in proportion to the extent to which the electrochemically active sites are blocked by the adsorbed inhibitor.

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 50–60 min from the moment of immersion. The inhibition efficiency expressed as percent inhibition ($\eta\%$) is defined as [23]:

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



where $I_{uninh.}$ and $I_{inh.}$ 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. 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 3. The data in exhibited that, the corrosion current density (I_{corr}) decreases, and the inhibition efficiency ($\eta\%$) increases as the concentration of inhibitor 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 surfactant molecule. The increase of inhibitor efficiency with increasing the concentration can be interpreted on the basis the adsorption amount and the coverage of surfactant molecule, increases with increasing concentration [24]. The E_{corr} of carbon steel shifted to the positive side by addition of surfactants I, II and III and the shift increased with increasing concentration of inhibitor, indicating that the inhibitor reduces the anodic reaction. It was explained that this shift in E_{corr} is due to active sites blocking effect that occurs when an inhibitor is added [25]. In the presence of inhibitors VI, V and VI, E_{corr} values 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_{corr} that is characteristic of anodic and anodic/cathodic inhibitor [25].

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 > V > IV > III > VI in the presence of 100 ppm of investigated inhibitors. 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.

Table 4: Corrosion parameters obtained from Tafel polarization for carbon steel in CO₂-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)	$-E_{corr}$ (mV (Ag/AgCl))	I_{corr} (mAcm ⁻²)	β_a (mVdec ⁻¹)	$-\beta_c$ (mVdec ⁻¹)	θ	$\eta\%$
Absence	0.0	687	0.389	44	107	---	---
I	25	677	0.040	43	106	0.82	89.51
	50	675	0.033	34	108	0.86	91.27
	75	671	0.024	45	113	0.89	93.60
	100	664	0.012	46	111	0.97	96.84
II	25	679	0.039	44	110	0.84	89.88
	50	678	0.032	44	105	0.87	91.59
	75	675	0.024	47	109	0.91	93.81
	100	667	0.011	43	114	0.97	96.94
III	25	683	0.079	44	111	0.81	79.46
	50	681	0.069	49	109	0.85	82.17
	75	679	0.050	44	108	0.89	86.99
	100	677	0.044	42	105	0.97	88.66
IV	25	700	0.193	51	106	0.79	50.27
	50	693	0.125	47	113	0.84	67.77
	75	684	0.090	45	111	0.89	76.61
	100	687	0.032	42	110	0.95	91.73



V	25	691	0.146	40.	106	0.67	62.38
	50	683	0.095	43	103	0.74	75.53
	75	690	0.069	45	106	0.82	82.17
	100	685	0.025	47	104	0.91	93.54
VI	25	690	0.095	47	108	0.73	75.37
	50	680	0.083	46	105	0.78	78.66
	75	695	0.060	45	106	0.84	84.47
	100	683	0.052	46	113	0.92	86.50

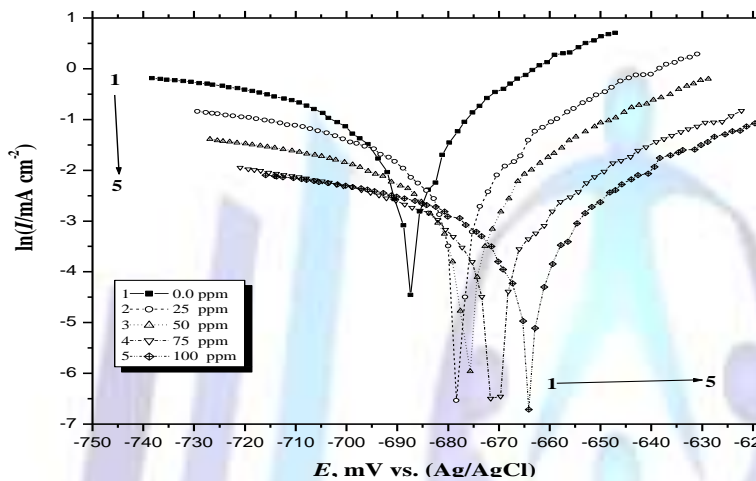


Fig. 1: Tafel polarization curves for carbon steel in CO₂-saturated brine containing different concentration of inhibitor (I) at 50 °C.

LPR Corrosion Rate

LPR test has been performed in brine saturated with CO₂ at 50 °C, in turbulence fluid stream during 20 hours. Figures 2 and 3 show that, the change in corrosion rate (CR) with time for carbon steel in CO₂-saturated 1%NaCl solution containing different concentrations form inhibitors **I** and **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. 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⁺ [26]. 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 [27].

Variation of the corrosion rate for inhibitors **I** and **V** at different concentrations are presented in Figures 2 and 3. 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:

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

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

where CR₀ 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 inhibitors, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 87.37 and 97.91 % at 100 ppm after 20 hour of exposure (Table 5). 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.

Table 5 shows the calculated values of corrosion rates, the inhibition efficiencies and the surface coverage in the absence and presence of different concentrations of different inhibitors at 50 °C. The data exhibited that, the corrosion rates, the inhibition efficiencies and the surface coverage are found to depend on the concentrations of the inhibitors. The corrosion rate (CR) are decreased, and the inhibition efficiencies (η %) and the surface coverage (θ) 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. 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 > V > IV > III > VI. 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 CO₂- saturated 1% NaCl solution in the presence of studied complex surfactants can be attributed to the formation of a protective film of iron carbonate (FeCO₃) in the metal surface [14]. 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 carbon steels in CO₂-saturated solutions. Ogundele and White suggested that, iron carbonate, FeCO₃, may be important in the formation of protective layers on steel surface [28]. The formation of iron carbonate can be explained by using the following Eq.[14].



By comparison between inhibition efficiency values (η %) which are calculated from both LPR corrosion rate and extrapolation of anodic and cathodic curves, we find that both have similar trend. In other words, the inhibition efficiency increases with increasing surfactant concentration, and the maximum inhibition efficiency values are obtained at 100 ppm in the case of all investigated complexes. It is noteworthy that, the values of inhibition efficiency obtained by LPR corrosion rate results are greater (Table 5) than those obtained by cathodic and anodic extrapolation curves (Table 4). Such results can be attributed to the different interaction of surfactant molecule with the metal surface during cathodic and anodic polarization.

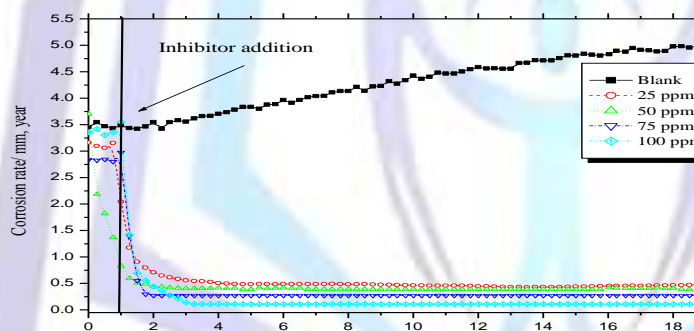


Figure 2: Variation of the Corrosion rate with time for carbon steel in CO₂-saturated 1 % NaCl solution containing different concentrations of inhibitor I at 50 °C.

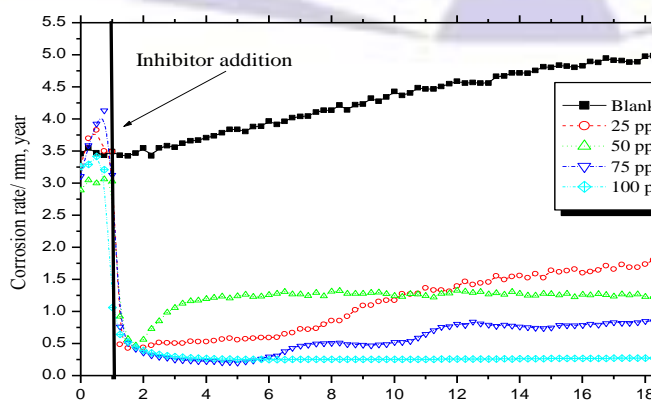


Figure 3: Variation of the Corrosion rate with time for carbon steel in CO₂-saturated 1 % NaCl solution containing different concentrations of inhibitor V at 50 °C.



Table 5: The corrosion parameters obtained from LPR corrosion rate measurements for mild steel electrode in CO₂-saturated brine in the absence and presence of various concentrations of investigated surfactants at 50 °C.

Inhibitors code	Concentration, ppm	Corrosion rate (mm/year)	Surface coverage θ	The inhibition efficiency, $\eta\%$
Absence	0.0	5.037	-----	-----
I	25	0.483	0.90	90.41
	50	0.393	0.92	92.19
	75	0.275	0.94	94.54
	100	0.110	0.97	97.81
II	25	0.464	0.91	90.78
	50	0.377	0.93	92.51
	75	0.264	0.95	94.75
	100	0.105	0.98	97.91
III	25	0.994	0.80	80.26
	50	0.856	0.83	83.00
	75	0.611	0.87	87.86
	100	0.526	0.89	89.55
IV	25	2.479	0.50	50.78
	50	1.589	0.68	68.45
	75	1.139	0.77	77.38
	100	0.370	0.92	92.65
V	25	1.863	0.63	63.01
	50	1.194	0.76	76.29
	75	0.856	0.83	83.00
	100	0.278	0.94	94.48
VI	25	1.202	0.76	76.13
	50	1.035	0.79	79.45
	75	0.739	0.85	85.32
	100	0.636	0.87	87.37

Surface tension and surface active properties

The main importance of the critical micelle concentration (CMC) consists of the fact that at this concentration, most of the physical and chemical properties of the surfactant solutions present an abrupt variation. The values of surface tension (γ) were measured at 303 K for various concentrations of the mixed emulsifiers. The measured values of (γ) were plotted against \ln of the surfactant concentration, $\ln C$ (Fig. 4). The intercept of the two straight lines designates the CMC, where saturation in the surface adsorbed layer takes place. The surface active properties of the surfactant, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}), and minimum area per molecule (A_{min}) were calculated using the following equations [29]

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{5}$$

$$\Gamma_{max} = \frac{-1}{RT[\partial\gamma/\partial\ln C]_T} \tag{6}$$

$$A_{\min} = \frac{1}{\Gamma_{\max} \times N_A} \quad (7)$$

$$\Delta G_{mic}^o = RT \ln CMC \quad (8)$$

$$\Delta G_{ads}^o = \Delta G_{mic}^o - 0.6023\pi_{CMC} A_{\min} \quad (9)$$

Where $\partial\gamma/\partial\ln C$ is maximum slope, γ_0 is the surface tension of pure water, γ_{CMC} the surface tension at critical micelle concentration, N_A is the Avogadro's number (6.023×10^{23} molecules/mol), R is the molar gas constant ($R= 8.314$ J/(mol K)) and T is the absolute temperature = ($t^\circ\text{C}+273$), ΔG_{mic}^o is the Gibbs free energy of micellization, ΔG_{ads}^o is the Gibbs free energy of adsorption [30].

The data presented in Table 6 show some of the surface active properties for the investigated surfactants. The results indicate that, the consequent increase in of Γ_{\max} leads to crowding at the interface, which causes a decrease in A_{\min} values. The values of effectiveness (π_{CMC}) at 298 K indicate that the prepared compounds gives large reduction of surface tension at CMC, so that, these compounds acts as effective corrosion inhibitors for carbon steel in CO_2 - saturated 1% NaCl solutions.

The free energy changes of micellization and adsorption showed negative sign showing the spontaneity of the two processes at 25 °C (Table 6). Moreover, ΔG_{ads}^o increase in negativity than ΔG_{mic}^o . That showed the higher tendency of these surfactants towards adsorption rather than micellization. Then the adsorption will be accompanied with micellization at last. The tendency towards adsorption was referred to the interaction between the aqueous phases and the hydrophobic chains which pump the surfactant molecules to the interface [16].

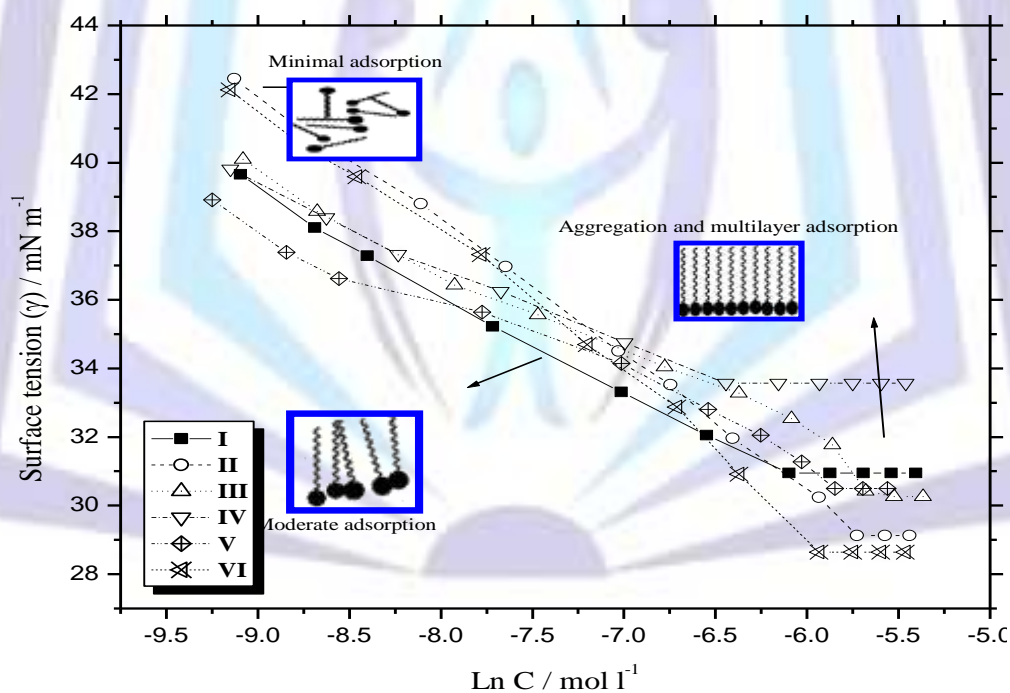


Fig. 4: Change of surface tension (γ) with the concentration of the surfactants at 25 °C.

**Table 6** The critical micelle concentration and surface parameters of the synthesized inhibitors.

Inhibitor	CMC $\times 10^{-3}$ (mol/l)	γ_{cmc} (mN m ⁻¹)	π_{cmc} (mN m ⁻¹)	Γ_{max} (mol cm ⁻²) $\times 10^{-10}$	A_{min} (nm ²)	ΔG_{mic}^o	ΔG_{ads}^o
I	2.24	30.95	41.85	4.47	0.29	-16.19	-31.9
II	3.25	29.13	43.67	6.24	0.20	-16.46	-32.4
III	3.41	30.42	42.38	6.81	0.29	-14.80	-29.2
IV	3.18	33.57	39.23	4.81	0.17	-15.80	-31.1
V	2.88	30.5	42.30	7.43	0.17	-16.33	-32.2
VI	2.64	28.64	44.16	6.69	0.21	-14.66	-28.9

Adsorption isotherm

The relation between C/θ and C at 323 K was shown in Fig. 5. A linear relation can be found between C/θ and C . The slope and the intercept were calculated. The slope was near unity. This behavior indicates that the adsorption of surfactants on carbon steel surface obeys Langmuir adsorption isotherm indicating that the inhibitor molecules were adsorbed on the metal surface and form a barrier, which isolated the metal surface from the electrolyte [31]. The slope of the isotherm deviates from unity as expected. This deviation may be explained on the basis of interaction between the adsorbed species on the metal surface by mutual repulsion or attraction [17].

The adsorption–desorption equilibrium constant K_{ads} values could be calculated from the intercepts of the straight lines on the C_{inh}/θ -axis, the K_{ads} was related to the standard free energy of adsorption, ΔG_{ads}^o ; with the following equation

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right) \quad (10)$$

The high value of the adsorption–desorption equilibrium constant as represented in Fig. 6, reflects the high adsorption ability of this inhibitor on the carbon steel surface [16].

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 -25.91 and -19.54 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 physisorption was supposed. The negative values of ΔG_{ads}^o indicate a spontaneous adsorption of the surfactants on the surface of investigated electrode [16]. The ΔG_{ads}^o for inhibitor II (-25.91 kJ/mol) was less than other surfactants which indicate the stronger adsorption for inhibitor II more than other surfactants.

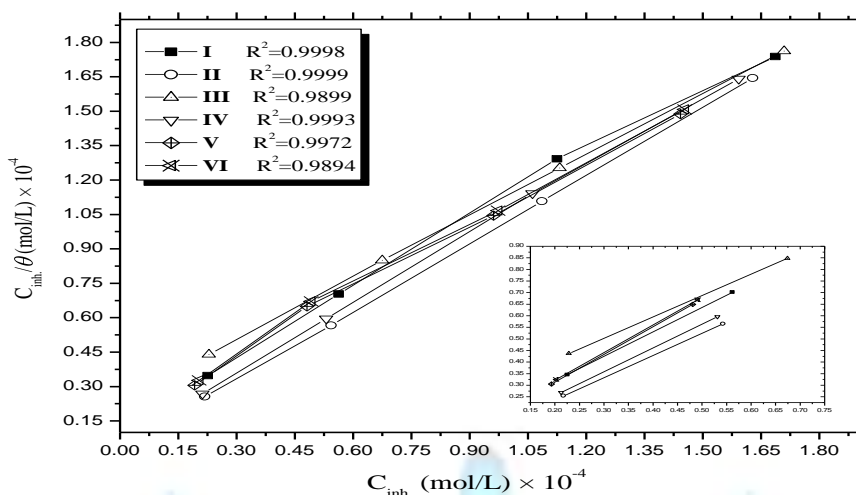


Figure 5: Curve fitting of the corrosion data obtained from LPR corrosion rate measurements for carbon steel in CO₂ saturated brine containing various concentrations of inhibitors according to Langmuir adsorption isotherm

CONCLUSIONS

The conclusion could be drawn in the following points:

1. The inhibition properties of some new surfactants were tested by using LPR corrosion rate and potentiodynamic polarization measurements. According to the results, the prepared surfactants were good inhibitors for carbon steel in CO₂-saturated 1.0 % NaCl solution.
2. The protection efficiency increased with increasing inhibitor concentration, getting maximum values ranged between 87.37 and 97.91 % at 100 ppm after 20 hour of exposure.
3. The relative efficiencies of the three compounds studied in 1% NaCl solution saturated with CO₂ at 50 °C were found to be in the following order: **II > I > V > IV > III > VI**.
4. Polarization curves showed that the inhibitors **I, II and III** and reduces the anodic reaction, but inhibitors **VI, V and VI** was a mixed type.
5. The more negative values of free energies for adsorption (ΔG_{ads}^0) than free energies for micellization (ΔG_{mic}^0) show that the investigated surfactants favor adsorption to micellization.
6. Adsorption of the inhibitor molecule onto carbon steel surface obeys Langmuir isotherm.

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