

## Prediction and Measurements of Corrosion Inhibition of Mild Steel C1018 using Some Natural Naphthenate Surfactants in CO<sub>2</sub>-Saturated NaCl Solution

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**Abstract:** The efficiency of two natural naphthenate surfactants (Naphthenic-dimethylamine and Naphthenic-diethylamine complexes) as corrosion inhibitors for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution has been determined by linear polarization resistance corrosion rate and potentiodynamic polarization measurements. These compounds inhibit corrosion even at very low concentrations (25 ppm) and Naphthenic-diethylamine complex is the best inhibitor giving maximum inhibition efficiency 99.76 at 100 ppm. Polarization curves indicate that the two investigated compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. Adsorption of naphthenates surfactants on the mild steel surface is in agreement with the Langmuir Adsorption Isotherm Model and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Energy Dispersive X-Ray Fluorescence microscopy (EDRF) observations confirmed the existence of such an adsorbed film on the mild steel surface.

**Key words:** Corrosion inhibition, natural naphthenate surfactants, mild steel, CO<sub>2</sub>-saturated solution, EDRF

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### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) corrosion of carbon steel pipelines and equipment in the oil and gas industry has been given much attention in recent years because of an increased tendency to inject CO<sub>2</sub> into oil wells to reduce the viscosity of oil and increase its production (Ikeda *et al.*, 1984; Jiang *et al.*, 2006). An important fact is that when CO<sub>2</sub> dissolves in water, carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is produced with the characteristic that is more aggressive than hydrochloric acid at the same pH (Zhang *et al.*, 2007). Despite the fact that carbon steel has low resistance to CO<sub>2</sub> environments, it is widely used in the petroleum industry mainly due to economical reasons (Jiang *et al.*, 2006). What makes feasible the use of carbon steels is the natural precipitation of protective iron carbonate (FeCO<sub>3</sub>) (Farelas *et al.*, 2010; Van Hunnik *et al.*, 1996). In order to reduce the corrosion of mild steel an alternative is to use inhibitor. The corrosion control by inhibitors is one of the most common, effective and economic methods to protect metals (Benali *et al.*, 2005; Machnikova *et al.*, 2008). Corrosion inhibition of carbon steel is a result of a barrier film forming between the carbon steel and the environment.

Surfactants are molecules composed of a polar hydrophilic group, the 'head', attached to a non-polar

hydrophobic group, the 'tail'. In general, in aqueous solution the inhibitory action of surfactant molecules may also be due to physical (electrostatic) adsorption or chemisorption onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface. The adsorption of the surfactants markedly changes the corrosion resisting property of a metal and for this reason, studies on the relation between adsorption and corrosion inhibition are of considerable importance (Bastidas *et al.*, 2003; Bolzan *et al.*, 2001; Stipnisek-Lisac *et al.*, 2002; Sahin *et al.*, 2002). The adsorption behavior of surfactants at the solid-solution interface is described by Luo *et al.* (1998) and Miller and Qutubuddin (1987). The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. Surfactants have been used for the corrosion inhibition of carbon steel in CO<sub>2</sub> environments (Abd El-Lateef, 2012a, b; Abbasov *et al.*, 2013a, b).

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for mild steel in CO<sub>2</sub>-saturated NaCl solution. An attempt was also made to clarify the effects of concentration of the studied surfactants on the inhibition efficiency. The measurements of corrosion rate and percentage inhibition

efficiency of different natural naphthenates surfactants towards corrosion of mild steel by linear polarization resistance corrosion rate and electrochemical polarization technique were performed in CO<sub>2</sub>-saturated solution in the absence and presence of the investigated surfactants in the concentration range (25-100 ppm). Energy Dispersive X-Ray Fluorescence (EDRF) was performed to verify the presence of the inhibitor on the carbon steel surface.

## MATERIALS AND METHODS

**Chemical composition of mild steel alloy:** The rotating disk working electrodes for tests were made of mild steel grade 080A15 and have an area of 4.55 cm<sup>2</sup> with a chemical composition (wt.%) C: 0.18%, Si: 0.17%, Mn: 0.70%, P: 0.011%, S: 0.03%, Ni: 0.0%, Cr: 0.01% and Fe: balance.

**Synthesis of surfactant inhibitors:** The surfactants used as inhibitors were synthesized in the laboratory based on petroleum acids and nitrogenous bases. The new series of the naphthenates surfactants were synthesized from naphthenic acids isolated from light oil fractions (T<sub>b</sub> = 180-350°C) (Samedov *et al.*, 2008). Naphthenic acids were taken at molar ratio 1:1 with dimethylamine and diethylamine. The components of reactions were mixed well for a period 30 min at 25°C. Two complex surfactants were synthesized in high purity by the compositions as shown in Table 1. The chemical structure of the synthesized surfactants was characterized by using FT-IR, Spectrum BX spectrometer using KBr disks.

**Preparation of solutions:** The aggressive solutions were made of AR grade 1% NaCl solutions saturated with carbon dioxide gas. The 1% NaCl solution was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was from 25-100 ppm used for corrosion measurements. All inhibitors solutions were prepared using distilled water.

**Corrosion measurements:** The measurements were performed on the rotating cylinder electrode (A = 4.55 cm<sup>2</sup>). This electrode was used for one time. The reference electrode was Ag/AgCl electrode to which all potentials are referred.

Table 1: List of the synthesized complex surfactants includes code number, name and structure

Code number of the inhibitor	Name and abbreviation	Structure
I	Naphthenic-Dimethylamine Complex (NDMC)	$[R-COO]N^+H_2 \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$
II	Naphthenic-Diethylamine Complex (NDEC)	$[R-COO]N^+H_2 \begin{matrix} \text{CH}_2-CH_3 \\ \text{CH}_2-CH_3 \end{matrix}$

Before beginning the experiment, the prepared 1% of sodium chloride solution was stirred by a magnetic stirrer for 30 min in 1000 mL cell. Then, this cell was thermostated at 50°C for 1 h 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 corrosion resistance of the investigated mild steel in 1% NaCl saturated with CO<sub>2</sub> was examined using two different techniques.

**Potentiodynamic measurements:** The potentiodynamic polarization curves were performed in a potential range ±100 mV with respect to corrosion potential (E<sub>corr</sub>) at temperature (50°C). Three electrodes were used consisting of a reference electrode (Ag/AgCl) a Working Electrode (WE) and a Counter Electrode (CE) at scan rate of 1 mV sec<sup>-1</sup>.

**Linear polarization resistance corrosion rate:** The Linear Polarization Resistance (LPR) corrosion rate bubble-test method involves evaluating the corrosion of steel in simulated brine saturated with CO<sub>2</sub> at a temperature equivalent to that in the field. 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 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/cm<sup>2</sup> 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 to +10 at 10 mV min<sup>-1</sup> around the rest potential is performed.

Each experiment was performed with freshly prepared solution. Measurements were conducted at 50°C for the investigated CO<sub>2</sub>-saturated 1% NaCl solution. For this purpose, Magnetic Stirrer with Heater (115 V, 50/60 Hz) was used.

**Surface analysis:** In order to observe any changes in surface morphologies of the mild steel samples after testing, the specimens were first immersed in the test media with and without an inhibitor for 3 days then cleaned with bi-distilled water and acetone and dried with

cool air. Then, the morphology of the tested sample was observed by using HORIBA XGT-7000-Energy Dispersive X-Ray Fluorescence (EDRF) a microscope with a system of partial/complete evacuation of the sample.

**RESULTS AND DISCUSSION**

**Chemical structure of the synthesized natural naphthenate surfactants:** The chemical structures for naphthenate surfactants were confirmed by FT-IR. The FT-IR absorption spectra for surfactant II showed an absorption band at the 2330/cm indicating that the amine band was disappearing by emerging ammonium ion (R-NH<sub>2</sub><sup>+</sup>). In addition, there was a strong band at 865/cm indicating the presence of CH<sub>2</sub> groups. The strong band at 1725/cm is indicating to C = O group. The increasing C = O group frequency due to occurring a link between the acid proton with the amino nitrogen that leads to increasing the attraction of electrons from carbonyl group. The FT-IR absorption spectra confirmed that the disappearance of -OH band of acid (broad band) this confirmed the transfer of proton of acid to nitrogen atom of amine to form -<sup>+</sup>NH<sub>2</sub>- group.

**Potentiodynamic polarization curves:** In order to study the effect of naphthenates surfactants on the polarization behavior of mild steel, polarization curves for different concentrations of surfactant II in CO<sub>2</sub>-saturated 1% NaCl solution at scan rate 1 mV sec<sup>-1</sup> and at 50°C was plotted (Fig. 1). Corrosion parameters were calculated on the basis of cathodic and anodic potential vs. current density characteristics in the Tafel potential region (El-Sayed *et al.*, 2010a, b). The values of the corrosion current density (I<sub>corr</sub>) for the mild steel in the absence and presence of investigated surfactants were determined by the extrapolation of the cathodic and anodic Tafel lines to corrosion potential (E<sub>corr</sub>). The inhibition efficiency is calculated by the following expression:

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

where, I<sub>uninh</sub> and I<sub>inh</sub> 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) CO<sub>2</sub>-saturated 1% NaCl solution at the same temperature. As can be seen that a marked shift in both cathodic and anodic branches of the polarization curves of mild steel towards lower current densities in the presence of surfactants molecule. This means that the surfactants 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 similar behavior was observed after the addition of inhibitor I to the CO<sub>2</sub>-saturated brine. It is also obvious that inhibitor II has higher inhibition efficiency than inhibitor I at all investigated concentrations.

The values of I<sub>corr</sub>, cathodic (β<sub>c</sub>) and anodic Tafel (β<sub>a</sub>) slopes obtained by fitting the polarization data in the vicinity of E<sub>corr</sub>±100 mV, E<sub>corr</sub>, degree of surface coverage (θ) and the inhibition efficiency (η%) obtained from Fig. 1 are listed in Table 2. The data exhibited that the

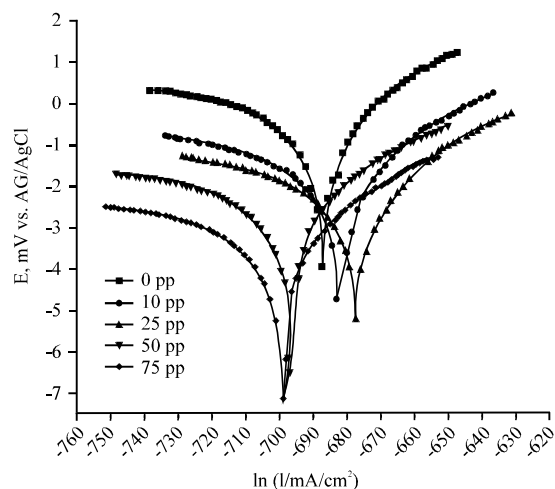


Fig. 1: Tafel polarization curves for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations of inhibitor (II) at 50°C

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

Inhibitors code	Conc. of inhibitor (ppm)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	-E <sub>corr</sub> (mV (Ag/AgCl))	β <sub>a</sub> (mV dec <sup>-1</sup> )	-β <sub>c</sub> (mV dec <sup>-1</sup> )	θ	η(%)
Absence	0	389.00	687	44	107	-	-
I	25	89.50	689	47	110	0.769	76.99
	50	72.85	685	49	116	0.812	81.27
	75	61.50	682	54	121	0.841	84.19
	100	21.78	693	61	125	0.944	94.40
II	25	54.73	682	50	108	0.859	85.93
	50	40.45	677	57	11	0.896	89.60
	75	21.16	695	62	119	0.945	94.56
	100	4.66	699	69	129	0.988	98.80

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  $I_{corr}$  was observed for inhibitor II. 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 (Akbarzadeh *et al.*, 2011; El-Sayed *et al.*, 2010a, b). 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  $CO_2$ -saturated 1% NaCl solution. This may be considered due to the mixed type behaviour of the studied inhibitors. It can be observed, the shift in  $E_{corr}$  that is characteristic of anodic and anodic/cathodic inhibitor (Lopez *et al.*, 2005). Moreover, the increases in the cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ) are related to

the decrease in both the cathodic and anodic currents. This indicates that natural naphthenate surfactants powerfully inhibit the corrosion process of the mild steel in the investigated media and its ability as a corrosion inhibitor is enhanced as its concentration. Conclusively, the surfactant inhibitor having near unity  $\theta$  (Table 2) was considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of carbon steel significantly.

Addition of natural naphthenates surfactants to the chloride solutions saturated with  $CO_2$  decreases the currents density significantly and the increase in its concentration is shown to increase the effect. This provides another confirmation of the ability of surfactant molecule to be adsorbed by forming a protective layer on the steel surface and to prevent it from corrosion.

**LPR corrosion rate:** LPR test has been performed in brine saturated with  $CO_2$  at  $50^\circ C$ , in turbulence fluid stream during 20 h. Figure 2 shows that the change in Corrosion

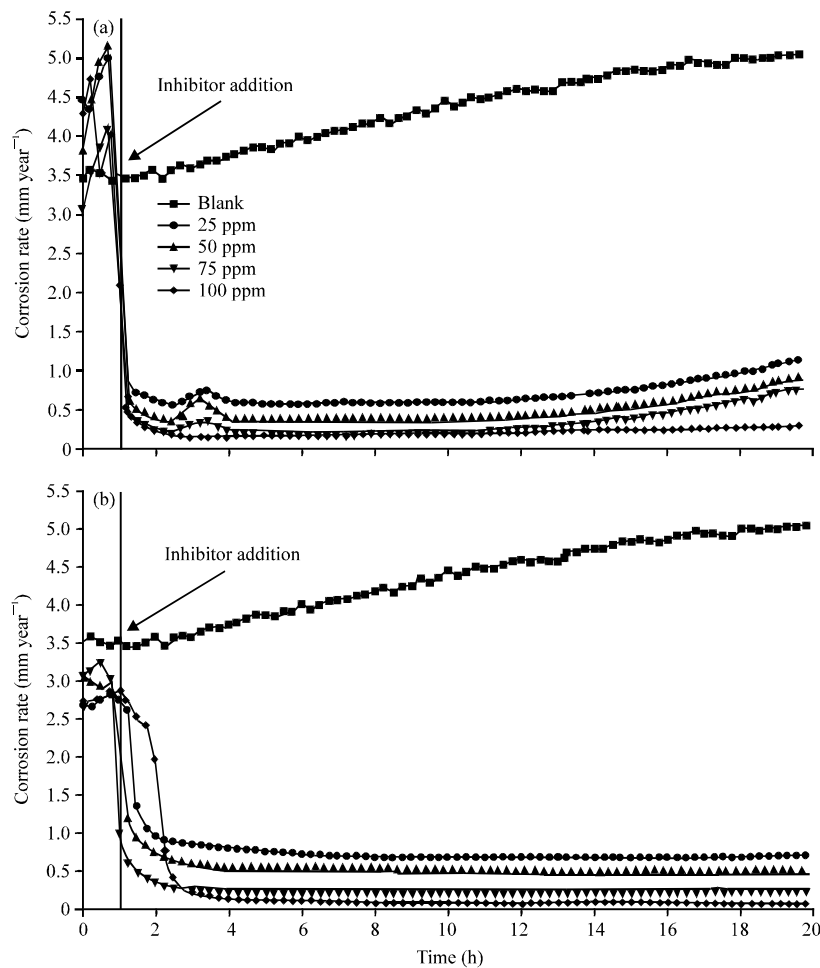


Fig. 2: Variation of the corrosion rate with time for mild steel in  $CO_2$ -saturated 1% NaCl solution containing different concentrations of inhibitors; a) I; b) II at  $50^\circ C$

Rate (CR) with time for carbon steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations form inhibitors I and II at 50°C. The inhibitor was added after 1 h 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 year<sup>-1</sup>. It can be observed from Fig. 2 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 (Fe<sub>3</sub>C) 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 Fe<sup>2+</sup> (Staicopolus, 1963). Fe<sub>3</sub>C is part of the original steel in the non-oxidized state and accumulates on the surface after the preferential dissolution of ferrite (α-Fe) into Fe<sup>2+</sup>. Depending on the microstructural properties of the steel, the morphology of these carbides will be different (laminar, globular, etc.) influencing the behavior of the material in a corrosive media. Because the carbide phase could reinforce a protective layer and anchor it to the steel substrate, the size and distribution of these carbides become very important. 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 (Crolet *et al.*, 1998; Videm *et al.*, 1996).

Variation of the corrosion rate for inhibitors I and II at different concentrations are presented in Fig. 2. Corrosion parameters were calculated on the basis of LPR corrosion rate test. The inhibition efficiency (η%) was calculated according to the following equations (Abd El-Lateef *et al.*, 2012a):

$$\eta\% = \frac{CR_0 - CR_1}{CR_0} \times 100 \quad (2)$$

Where:

CR<sub>0</sub> = The corrosion rate without inhibitor

CR<sub>1</sub> = The corrosion rate when inhibitor is present

It can be seen that the presence of inhibitors results a high decrease in the corrosion rate. In the case of these inhibitors, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency 95.27 and 99.76% at 100 ppm after 20 h of exposure for inhibitors I and II, respectively. 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 (Abbasov *et al.*, 2013a, b).

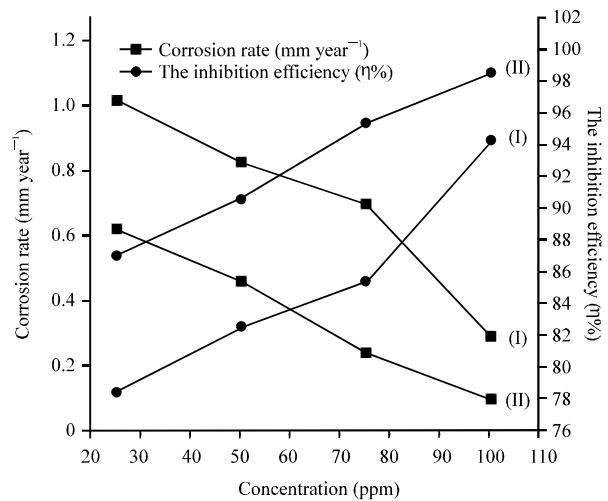
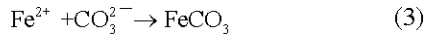


Fig. 3: Dependence of inhibition efficiency and corrosion rate of mild steel on the concentrations of inhibitors in CO<sub>2</sub>-saturated brine at 50°C

Figure 3 shows the calculated values of corrosion rates and the inhibition efficiencies in the absence and presence of different concentrations of different inhibitors at 50°C. The data exhibited that the corrosion rates and the inhibition efficiencies are found to depend on the concentrations of the inhibitors. The Corrosion Rate (CR) are decreased and the inhibition efficiencies (η%) are increased with the increase of the surfactant concentrations. This could be explained on the basis of inhibitor adsorption on the metal surface and the adsorption process enhances with increasing inhibitor concentration, formation of the barrier film which prevented aggressive medium from attacking the metal surface. The adsorption can occur either directly on the basis of donor-acceptor interaction between the unshared electron pairs and/or π-electrons of inhibitor molecule and the vacant d-orbitals of the metal surface atoms or by interaction of the inhibitors with already adsorbed chloride ions (Zhang *et al.*, 2009).

The high inhibition efficiency obtained in CO<sub>2</sub>-saturated 1% NaCl solution in the presence of studied surfactants can be attributed to the formation of a protective film of iron carbonate (FeCO<sub>3</sub>) in the metal 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 carbon steels in CO<sub>2</sub>-saturated solutions. Ogundele and White (1986) suggested that iron carbonate, FeCO<sub>3</sub>, may be important in the formation of protective layers on steel surface. The formation of iron carbonate can be explained by using the following Eq. 3 (Abd El-Lateef *et al.*, 2012a, b):



By comparison between inhibition efficiency values ( $\eta\%$ ) which are calculated from both LPR corrosion rate and extrapolation of anodic and cathodic curves, researchers 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 inhibitors. It is noteworthy that the values of inhibition efficiency obtained by LPR corrosion rate results are greater than those obtained by cathodic and anodic extrapolation curves. Such, results can be attributed to the different interaction of surfactant molecule with the metal surface during cathodic and anodic polarization.

It is clear that the  $\eta\%$  values increased and that the CR values decreased with increasing inhibitor concentration. This result indicates a decrease in the active surface area caused by the adsorption of the inhibitors on the mild steel surface and it suggests that the corrosion process became hindered this hypothesis is corroborated by the anodic and cathodic polarization curves and the corrosion potential results. The best result for the inhibition efficiency of inhibitors was obtained with the diethylamine complex with efficiency equal to 97.76% at a concentration of 100 ppm. Researchers did not perform the analyses with high concentrations for the surfactant because at 100 ppm this inhibitor already produced a good result for inhibition efficiency. The efficiency of the dimethylamine complex was 95.27% at the same concentration.

**Adsorption isotherm:** The surface coverage,  $\theta$ , was calculated using the following equation (Hegazy and Zaky, 2010):

$$\theta = \frac{I_{\text{uninh.}} - I_{\text{inh.}}}{I_{\text{uninh.}}} \quad (4)$$

The values of the degree of surface coverage ( $\theta$ ) obtained from polarization measurements for the tested inhibitors have been applied to different adsorption isotherms. Since, adsorption isotherms can provide important clues to the nature of metal-inhibitor interaction it was established isotherms that describe the adsorptive behavior of the studied corrosion inhibitors. The best correlation among the experimental results was found to fit the Langmuir adsorption isotherm as shown in Fig. 4. Plotting  $C_{\text{inh}}/\theta$  versus  $C_{\text{inh}}$  yielded a straight line with a correlation coefficient ( $R^2$ ) higher than 0.998 and a slope closed to 1 according to the following equation (Abd El-Maksoud and Fouda, 2005):

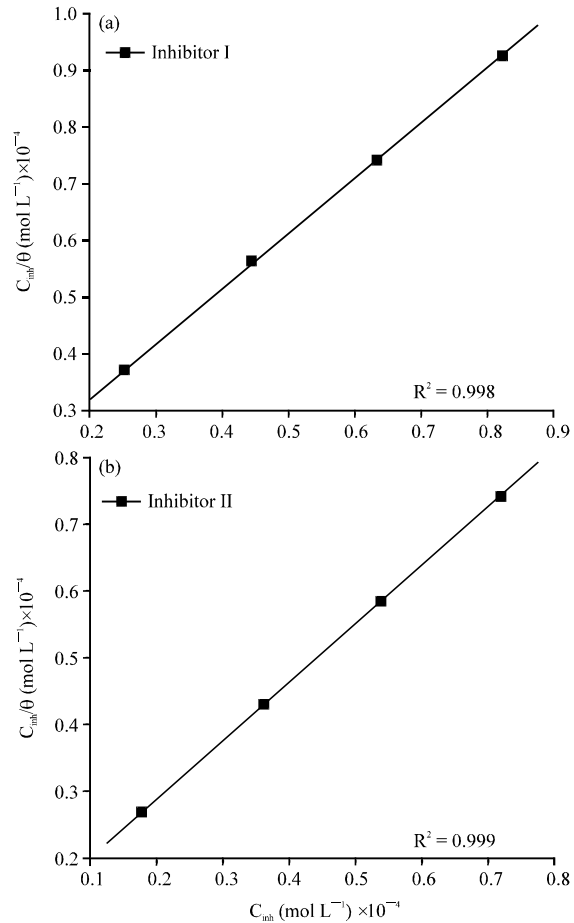


Fig. 4: Langmuir plots for a) inhibitors I and b) II in  $\text{CO}_2$ -saturated brine obtained from polarization measurements at  $50^\circ\text{C}$

$$\frac{C_i}{\theta} = \frac{1}{K_{\text{ads}}} + C_i \quad (5)$$

Where:

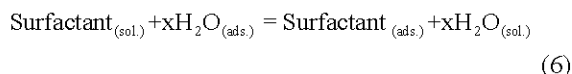
$C_{\text{inh}}$  = The inhibitor concentration

$K_{\text{ads}}$  = The adsorption equilibrium constant of the inhibitor on carbon steel surface

This indicates that the adsorption of these surfactants can be fitted to a Langmuir adsorption isotherm. The strong correlation of the Langmuir adsorption isotherm may confirm the validity of this approach. The equilibrium constant ( $K_{\text{ads}}$ ) for the adsorption-desorption process of these compounds can be calculated from reciprocal of the intercept. The adsorptive equilibrium constant ( $K_{\text{ads}}$ ) values are  $11.8 \times 10^5$  and  $13.5 \times 10^5 \text{ M}^{-1}$  for inhibitors I and II, respectively. It is clear that the large values indicate a strong adsorption of the synthesized surfactants on the surface of mild steel in  $\text{CO}_2$ -saturated 1% NaCl solution. This may be due to the

formation of coordinated bonds between the unshared electron pairs and/or  $\pi$ -electrons of inhibitor molecule and the d-orbital of iron on the surface of steel.

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 ( $H_2O$ ) 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<sub>(sol.)</sub>] and water molecules at the electrode surface [ $H_2O_{(ads)}$ ]:



where, x is the size ratio that is the number of water molecules replaced by one organic inhibitor. The free energy of adsorption ( $\Delta G_{ads}^\circ$ ) of the inhibitor on carbon steel surface was calculated as follows (Badawi *et al.*, 2010):

$$\Delta G_{ads}^\circ = -2.303RT \log(55.5K_{ads}) \quad (7)$$

The values of  $\Delta G_{ads}^\circ$  are  $-48.3$  and  $-48.7$   $\text{kJ mol}^{-1}$  for inhibitors I and II, respectively. The negative values of indicate the spontaneous adsorption of the prepared

inhibitors on mild steel surface (Abd El-Maksoud and Fouda, 2005). Generally, values of  $\Delta G_{ads}^\circ$  up to  $-20$   $\text{kJ mol}^{-1}$  are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than  $-40$   $\text{kJ mol}^{-1}$  involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (Abdallah, 2002). The obtained values of the adsorption free energy,  $\Delta G_{ads}^\circ$ , were found to be  $>-40$   $\text{kJ mol}^{-1}$  are indicative of chemisorption (Szkłarska-Smiałowska, 1978).

**Surface analysis:** In order to see if the surfactant molecules are indeed adsorbed on the mild steel surface we carried out the EDRF with a microscope system analyses. Figure 5a shows an EDRF spectroscopy for mild steel surface in the investigated solution without inhibitors, exhibits the characteristics peaks are related to Fe, Mn, P, Cr and oxygen elements. This indicated that the corrosion product on mild steel surface being metal oxide. However, the data in Fig. 6a in the presence of 100 ppm of inhibitor II shows additional peaks characteristic of N element. This result proved that the adsorption of inhibitor molecule on mild steel surface leads to a decrease of the corrosion layer and higher concentration of the inhibitor is necessary to delay the corrosion process.

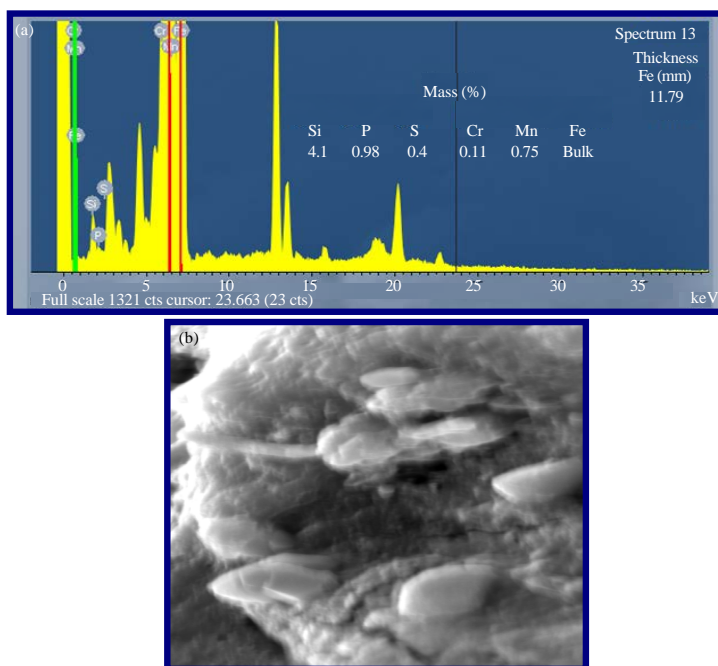


Fig. 5: EDRF analysis of mild steel electrode surface after immersion in  $CO_2$ -saturated; a) 1% NaCl for 3 days without inhibitors and b) the picture at the same conditions

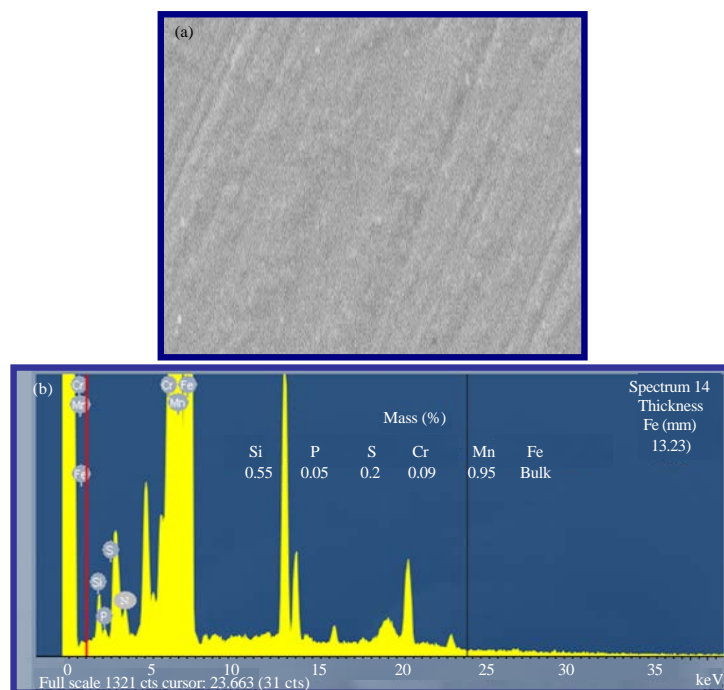


Fig. 6: EDRF analysis of mild steel electrode surface after immersion in CO<sub>2</sub>-saturated solution containing 100 ppm inhibitor II for; a) 3 days and b) the picture at the same conditions

From quantitative analysis, it can be observed that the mass thickness of iron for the electrode surface is 12.75 mm. In the aggressive media without inhibitors, there is a decrease in the mass thickness of iron on the electrode surface after corrosion process (11.79 mm) but in the presence of 100 ppm of inhibitor II, the mass thickness increased to 13.23 (Fig. 5a and 6b). The quantitative analysis showed that the presence of inhibitor in CO<sub>2</sub>-saturated brine an adsorbed layer is formed on the electrode surface which successfully inhibits corrosion processes. Figure 5b shows a photograph recorded for mild steel surface after immersion in CO<sub>2</sub>-saturated 1% NaCl solutions for 3 days in the absence inhibitors, the results exhibited that thick porous layer of corrosion product covered all electrode surfaces, disclosing that in free corrosive solution, the surface is highly corroded. In case of mild steel immersed in CO<sub>2</sub>-saturated 1% NaCl solutions in the presence of 100 ppm of inhibitor II (NDEC) at the same conditions, a smooth surface was noticed (Fig. 6b) which indicates a good protective film present on the mild steel surface. These results corroborate the potentiodynamic polarization and LPR corrosion rate measurements.

### CONCLUSION

LPR corrosion rate and Tafel polarization methods are used to study corrosion of mild steel in CO<sub>2</sub>-saturated 1%

NaCl solution and the inhibiting effect of two natural naphthenates surfactants. LPR corrosion rate measured within 20 h shows that all studied compounds act as inhibitors in the investigated medium. The highest inhibition efficiency is obtained by compound II (99.76% at 100 ppm).

Analysis of the polarization data show that the inhibiting properties increase with inhibitor concentration. The inhibition efficiency of inhibitor II was found to be more than those of inhibitor I for all concentrations. Polarization curves indicate that the two investigated surfactants are mixed inhibitors.

It is found that the inhibition occurs through adsorption which obeys the Langmuir adsorption isotherm. Calculated gibbs free energy of adsorption confirms the chemical nature of the adsorption. 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 naphthenates surfactants.

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