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The Effect of Non-ionic Surfactant on the Corrosion Inhibition of X52 Pipeline Steel in NaCl solutions

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Non-ionic NPE-4 surfactant was evaluated in X52 steel/2.453 wt% NaCl interface using electrochemical impedance spectroscopy (EIS) and polarization curves. The application of negative potential on steel surface and hydrodynamic condition were considered in order to study the adsorption process. Surfactant tested as corrosion inhibitor after electrochemical techniques displayed low corrosion rate values. Standard free energy indicated that the cathodic charge helped to adsorb physically the molecule on the metal surface. Thus, the molecule cathodically active was able to remove the corrosive species and blocked the active sites from metallic surface.

Keywords: Surfactant, X52 steel, impedance, polarization curves, cathodic charge.

1. INTRODUCTION

The corrosion process of the carbon steel in aqueous environments is a very important scientific and technological topic in the oilfield industry [1-3]. Actually, the oil recovery in México is every time more difficult due to the different qualities of the petroleum. Indeed, the transportation of heavy and extra-heavy petroleum is more complicated. In addition, the deposited sediment and solids dissolved can provoke the increase of the viscosity in the petroleum. The formation of heavy and extra-heavy oil presents important challenges that require significant technological developments in the oil industry. Furthermore, the petroleum viscosity effect is very detrimental on the internal of the pipeline steel surface during the operating conditions of the transportation process. One way to reduce the viscosity of the petroleum is the use of surfactants. So, the dosage of surfactant into heavy petroleum is able to improve its fluidity and transportation. In this manner, the chemical properties of NPE-4 surfactant have been applied in heavy and extra-heavy petroleum production [4]. Surfactant is defined as an active surface agent that is used as corrosion inhibitor in aqueous environment [5-10]. The surfactants are classified as anionic, cationic, non-ionic, or amphiphilic depending of its technological application such as detergents, wetting agents, emulsifiers and dispersants. However, the ionic character of the surfactant is due to the intrinsic properties [6, 7]. There are some studies associated to corrosion process on metallic surfaces and inhibition properties using surfactants [8-12]. One of them is the adsorption process study of different surfactants on aluminum surfaces in contact with HCl [8]. Another study reports the prediction of the inhibition corrosion process on mild steel in contact with 0.5 M NaCl and a non-ionic surfactant [10]. Studies on ionic, cationic or non-ionic surfactants mentioned above consider the electrochemical and physicochemical techniques for the characterization of adsorption process [12]. The aim of the present work is to investigate the inhibition effect of non-ionic NPE-4 surfactant in chloride solution on X52 pipeline steel at several interval of time, 30 °C in absence and presence of 600 rpm, as well as to study the cathodic charge effect on steel surface. To carry out this study the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were proposed because its versatility and was considerate to know the corrosion process in short time. First, the EIS characterization of the pipeline steel was performed in an aqueous solution mainly composed of 2.45% NaCl as blank. After, cathodic charge in order to study the adsorption process of the surfactant in X52 steel/chloride solution interface was considered. As a first approximation, the EIS analysis was made using equivalent circuits, where it is possible to discuss the modifications of the EIS diagrams with the presence of different process occurring simultaneously. Based on polarization curves, the adsorption and inhibition properties were evaluated. The electrochemical behavior were related to the modification of the stages involved in the corrosion process of the pipeline steel in the NaCl solution; obtaining a positive effect on the corrosion inhibition adding the surfactant and a contrary effect (dissolution of the steel) without the molecule in the conditions evaluated.

2. EXPERIMENTAL

2.1. Electrolyte media preparation

Solution test preparation was as follow: 2.45 g of NaCl were dissolved in 1000 mL of deionized water. This is a salt concentration considered for the preparation of synthetic ocean water recommended for standard test ASTM D1141 [13]. For the electrochemical impedance spectroscopy (EIS) evaluation, constant volume of 100 mL of 2.45 wt% NaCl (Blank solution) was used. Non-ionic surfactant commercially available called nonylphenol ethoxylate (387 g/mol) containing 4 length chain of ethylene oxide OE (NPE-4) in the hydrophilic region was used. The electronic structure, mesoscopic simulations and analytical characterization of NPE-4 molecule were reported in previous works [14]. The surfactant preparation was as follow: 0.3 g of molecule was dissolve in 10 mL of 2.45 wt% NaCl solution (solution B). Finally, 0.1 mL and 0.2 mL of solution B was added to blank solution to study the corrosion inhibition at 30 and 60 mgL^{-1} surfactant, respectively.

2.2. Cell and electrochemical evaluations

All electrochemical characterizations were carried out in an electrochemical cell with 4 electrodes arrangement as is shown in Fig. 1. The working electrode (WE) was a rod X52 pipeline steel. A steel surface area of 0.5 cm^2 was mechanical grinding using emery papers of grade 180, 240, 500 and 600 to obtain a flat, homogeneous and clean X52 steel surface. A rod graphite as auxiliary electrode (AE) and saturated calomel electrode (SCE) as reference electrode (RE) were used.

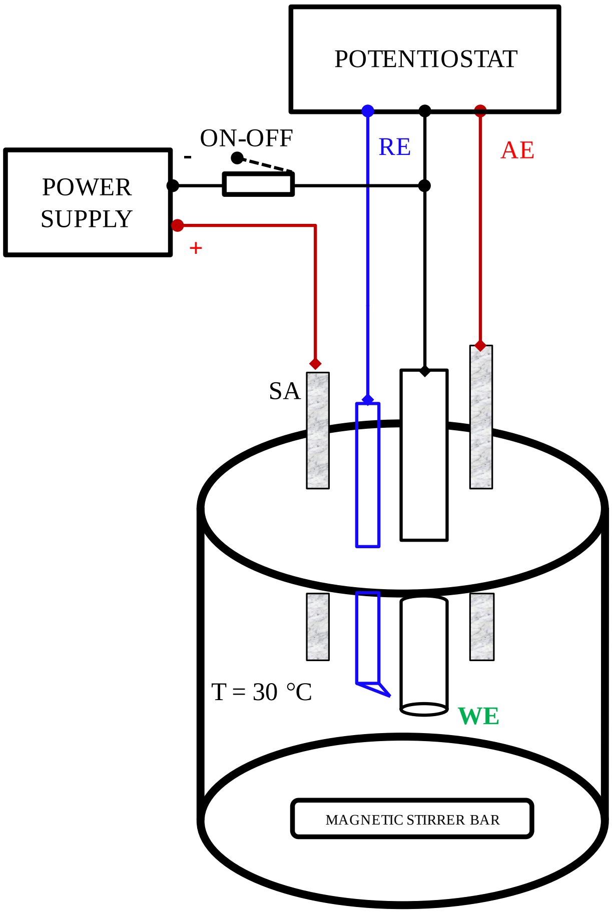


Figure 1. Experimental set-up.

The first electrochemical evaluation was carried out at open-circuit potential (OCP) and the second was applying a cathodic potential to obtain E_{corr} = -700 mV vs SCE using a power supply and second rod graphite as sacrificial anode (SA). The electrical arrangement of experimental equipment used in this work is similar to the cathodic protection methodology recommended by the ASTM G95 and G8 standards [15, 16]. Once set the electrical and electrochemical system, a magnetic stirring was introduced within the electrochemical cell in order to control a mechanical agitation at 600 rpm and temperature of 30°C.

2.3. Microstructure of the steel used

Nominal chemical composition of X52 pipeline steel is shown in Table 1. Fig. 2 shows a typical microstructure of the API X52 steel used in this study obtained by scanning electron microscopy (SEM). The structure consists of light areas (perlite) and the dark areas formed by ferrite. Perlite is formed by layers of ferrite and cementite. The average size grain of the microstructure is around 5-10 microns.

Table 1. Chemical composition of the API X52 pipeline steel (wt %)

C	Mn	Si	P	S	Cu	Cr	Ni	Nb	V	Ti	Al	Fe
0.08	1.05	0.26	0.019	0.003	0.019	0.02	0.02	0.041	0.054	0.002	0.038	Bal.

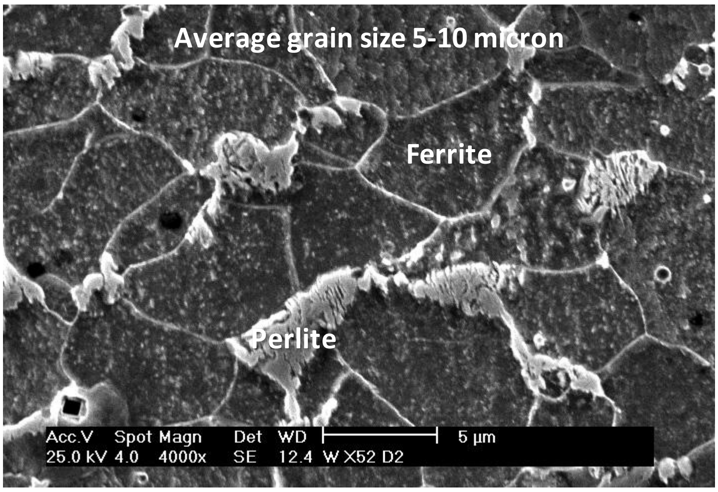


Figure 2. Typical microstructure of X52 steel obtained by SEM.

Low carbon steels generally have a ferrite-perlite structure containing little perlite. Additionally, is common that these steels contain sulphur forming manganese sulphide inclusions (MnS), which can be critical sites for initiate corrosion process.

2.4. Electrochemical parameter control

Potentiodynamic polarization curves were measured by potential scanning from ±300 mV vs OCP at a sweep rate of 1 mVs^{-1}. The electrochemical impedance spectroscopy tests (EIS) were obtained using 10 mV of perturbation and 10 kHz to 10 mHz of frequency after 1 and 15 h of exposition of the working electrode. In the case of -700 mV vs SCE, the impedance tests were evaluated after 1 h and disconnecting the power supply system (-700 mV OFF).

2.5. Hydrodynamic conditions

The hydrodynamic simulations of flow velocity in the laboratory were carried out through a magnetic stirrer, connecting the coupon to a Potentiostat/Galvanostat. The corrosion rate of the system was evaluated at static conditions and 600 rpm.

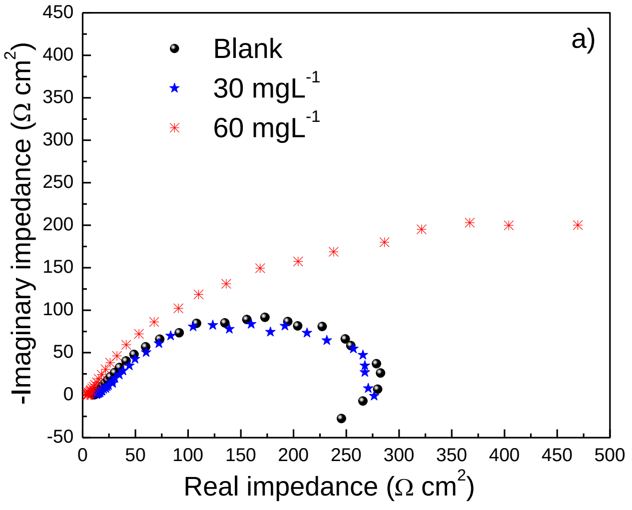
3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance spectroscopy (EIS)

The Nyquist diagrams obtained for X52 steel exposed to 2.45 wt% NaCl in the presence and absence of 30 and 60 mgL-1 of Non-ionic NPE-4 surfactant are shown in Fig. 3. Both characterization conditions (OCP and -700 mV) displaced the real and imaginary impedance toward higher values when surfactant concentration is increased; this behavior was recorded with -700 mV and two semicircles well defined were obtained.

The first semicircle generated under these conditions was the smaller, which is associated with the reduction and adsorption effect of the molecule surfactant. The magnitude of the second semicircle was the higher and its shape is associated to the diffusion process and the protective properties of the molecule [17]. In Fig. 3a, it can be noted that a depressed loop appears at intermediate frequencies. In the low region, inductive response is observed. This behavior can be mainly associated to the pitting, metal dissolution and formation of corrosion products from carbon steel surface as a consequence of the chloride solution.

The electrical parameters values were determined from Boukamp equivalent circuit software [17-20] in order to evaluate corrosion resistance associate with different process as the solution resistance (R_s), corrosion products resistance (R_{cp}), charge transfer resistance (R_{ct}) and/or the capacitance contribution (C) of film growth on the steel surface [20]. Fig. 4 shows the evolution of these parameters in function of the time.



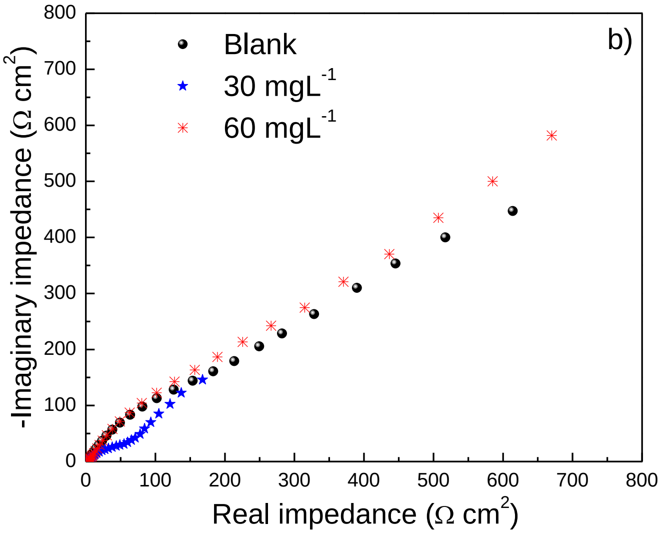
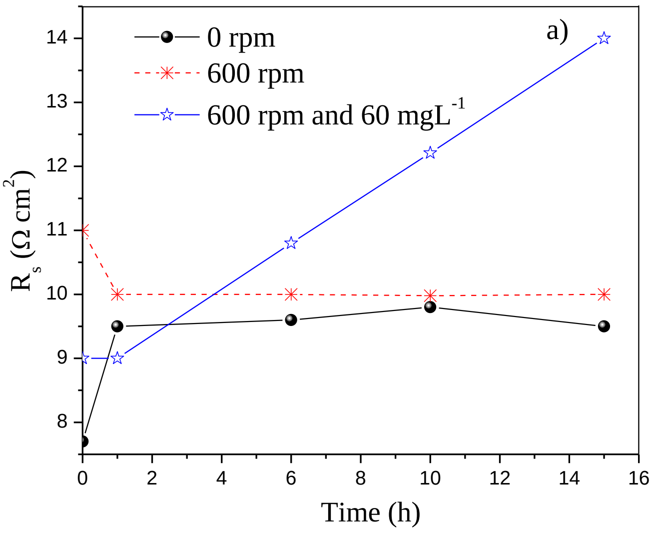


Figure 3. Nyquist diagrams obtained for X52 steel exposed to 2.45 wt% NaCl solutions and Non-ionic NPE-4 surfactant, after 1 h at 600 rpm and 30°C, a) OCP and b) -700 mV OFF.

Fig. 4a shows that the R_s values (R_s around 8-10 Ω cm^2) of X52 steel in 2.45 wt% NaCl obtained at static conditions and 600 rpm remained almost constant throughout all the time of evaluation. Meanwhile, adding 60 mgL^{-1} Non-ionic NPE-4 surfactant increases the R_s values over time. Indicating that surfactant modified the solution conductivity [18]. Fig. 4b shows that R_{cp} values obtained at 0 rpm increased with absence of stirring; while at 600 rpm decreased the R_{cp} values indicating that corrosion products are porous, soluble, and conductive [20-23]. In case of 60 mgL^{-1} surfactant the R_{cp} values were obtained between NaCl with and without stirring. The magnitudes of the R_{cp} values suggest the formation of corrosion products with non-protective properties (easily removed).



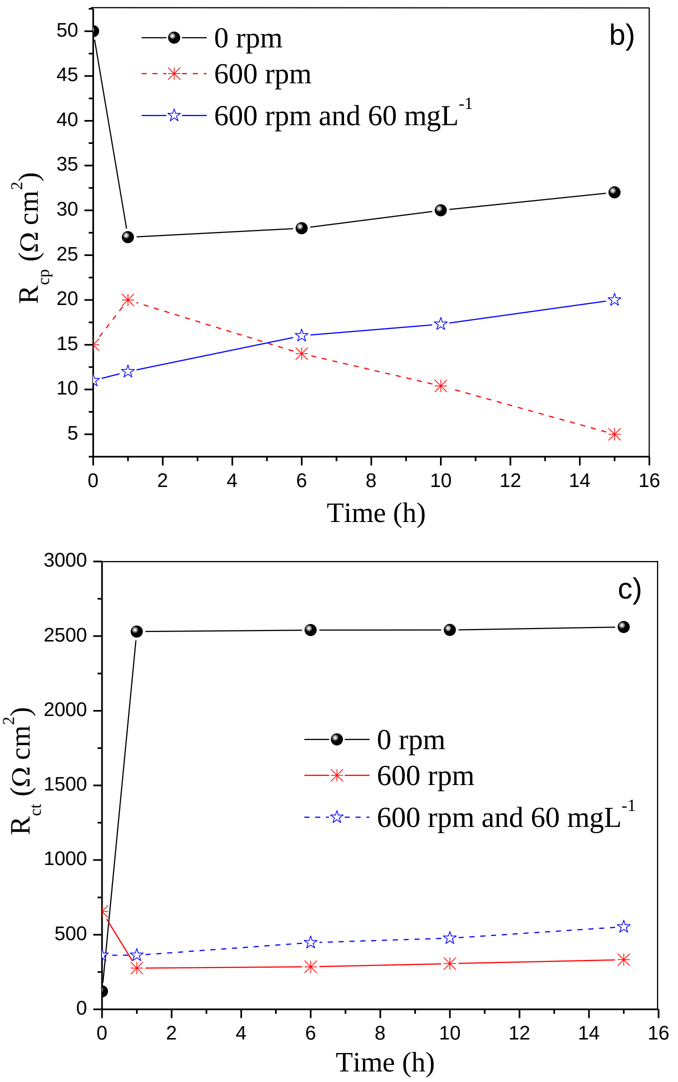


Figure 4. Resistance values in function of time for X52 steel exposed to 2.45 wt% NaCl solutions and 60 mgL^{-1} Non-ionic NPE-4 surfactant at OCP, after 1h and 30°C. a) Solution resistance, b) corrosion products resistance, c) charge transfer resistance.

Fig. 4c display that 2.45 wt% NaCl solution without agitation displaced the R_{ct} values toward higher values in all the time of evaluation; while a slight increase of R_{ct} values were observed when surfactant was added in X52 steel/NaCl interface. In order to include the influence of the cathodic charge, the pseudo-capacitance (C_i) values were evaluated using the following expression:

$$C_i = \frac{(Y_i R_i)^{\frac{1}{n_i}}}{R_i} \tag{1}$$

The terms Y_i and n_i were obtained using a constant phase element (CPE or Q) [21, 22]. The arrangement (Y_1R_1) was used to describe the corrosion product pseudo-capacitance, where the R_1 element was associated to the corrosion products resistance (R_{cp}). The arrangement (Y_2R_2) was used to describe the impedance diffusion response, where the R_2 element was associated to the diffusion of iron ions and surfactant molecule through the corrosion products (mainly iron oxides) to the solution from charge transfer resistance (R_{ct}) as shown in Table 2.

Table 2. CPE and pseudo-capacitance of deposit (C_1) and double layer (C_2) values of X52 in 2.45 wt% NaCl solution with and without Non-ionic NPE-4 surfactant after 1 h and 30°C.

	System	Y_1 ($Scm^{-2}s^{-n}$)	n_1	C_1 (μFcm^{-2})	Y_2 ($Scm^{-2}s^{-n}$)	n_2	C_2 (μFcm^{-2})
0 rpm	OCP(-0.599 mV)	4.94×10^{-4}	0.75	117	1.34×10^{-4}	0.93	124
	-700 mV OFF	2.99×10^{-3}	0.71	3550	1.28×10^{-2}	1	12800
	-700 mV OFF, 30 mgL^{-1}	1.98×10^{-5}	0.69	2589	1.20×10^{-2}	0.9	8756
	-700 mV OFF, 60 mgL^{-1}	1.87×10^{-5}	0.64	95.7	1.15×10^{-3}	0.8	429
600 rpm	OCP(-0.619 mV)	1.53×10^{-3}	0.65	234	1.1×10^{-3}	0.79	894
	OCP(-0.598 mV), 30 mgL^{-1}	1.41×10^{-3}	0.61	104	8.74×10^{-4}	0.80	699
	OCP(-0.498 mV), 60 mgL^{-1}	1.65×10^{-3}	0.72	370	6.37×10^{-4}	0.80	471
	-700 mV OFF	4.25×10^{-3}	0.60	216	4.41×10^{-4}	1	1060
	-700 mV OFF, 30 mgL^{-1}	5.51×10^{-3}	0.59	455	3.39×10^{-4}	0.96	370
	-700 mV OFF, 60 mgL^{-1}	3.1×10^{-3}	0.72	1620	4.15×10^{-4}	0.94	368

In this Table, it is observed for the blank increase in the C_1 values can be related with the behavior of porous iron oxides and C_2 is associated to diffusion process in the electrical double layer. Moreover, was observed that 0 rpm changed C_1 and C_2 toward lower values when surfactant concentration is increased using -700 mV OFF. Result indicates that the cathodic charge modified the energetic barrier and corrosion products (iron oxides) were removed. However, in presence of 600 rpm, it seems that the energetic barrier properties are different because this C_1 increased; indicating the presence of adsorption of surfactant. The surfactant adsorption process displaced the C_2 toward lower values when surfactant concentration was increased; indicating the formation of a more resistive film probably mixed by iron oxides and/or surfactant compound. This behavior could be linked to a greater removal of corrosion products and the diffusion of the molecule that block the active sites on metal surface. Thus, $C_2 = 368\ \mu Fcm^{-2}$ is associated to reducing the active area and the removal of iron oxide.

3.2. Potentiodynamic polarization curves

The polarization curves for X52 steel exposed to 2.45 wt% NaCl solutions with and without surfactant are shown in Fig. 5. NPE-4 surfactant displaced the corrosion current density (i_{corr}) towards lower values when surfactant dosage is increased in both OCP and -700 mV OFF conditions. Corrosion rate (CR) was determined from i_{corr} using equation 2 [24]. i_{corr} of the blank and surfactant was calculated by the intersection of the extrapolated cathodic and anodic Tafel lines at the experimentally measured OCP and -700 mV OFF from corrosion potential (E_{corr} vs SCE).

$$CR(\frac{mm}{year}) = \frac{i_{corr}A_w}{zF\rho} = 1159.57206 * i_{corr} \qquad (2)$$

For the X52 steel, the following values were used: atomic weight A_w = 55.85 g.mol^{-1}, z = 2 electrons, F = 96500 A.s.mol^{-1} and density ρ = 7.87 g.cm^{-3}.

E_{corr}, i_{corr}, Tafel slopes of the anodic (β_a) and cathodic (β_c) branches and CR were determined with and without surfactant and are shown in Table 3. In this Table, it is observed that the corrosive solution is affected by the addition of surfactant, which in turns changes the E_{corr} towards more negative potentials values. Furthermore, the presence of surfactant considerably changed β_c branch. CR and β_c indicate that the surfactant acted as corrosion inhibitor and modified the actives sites and cathodic reaction on steel surface, which may happen by chemical, physical or adsorption by electrical effect.

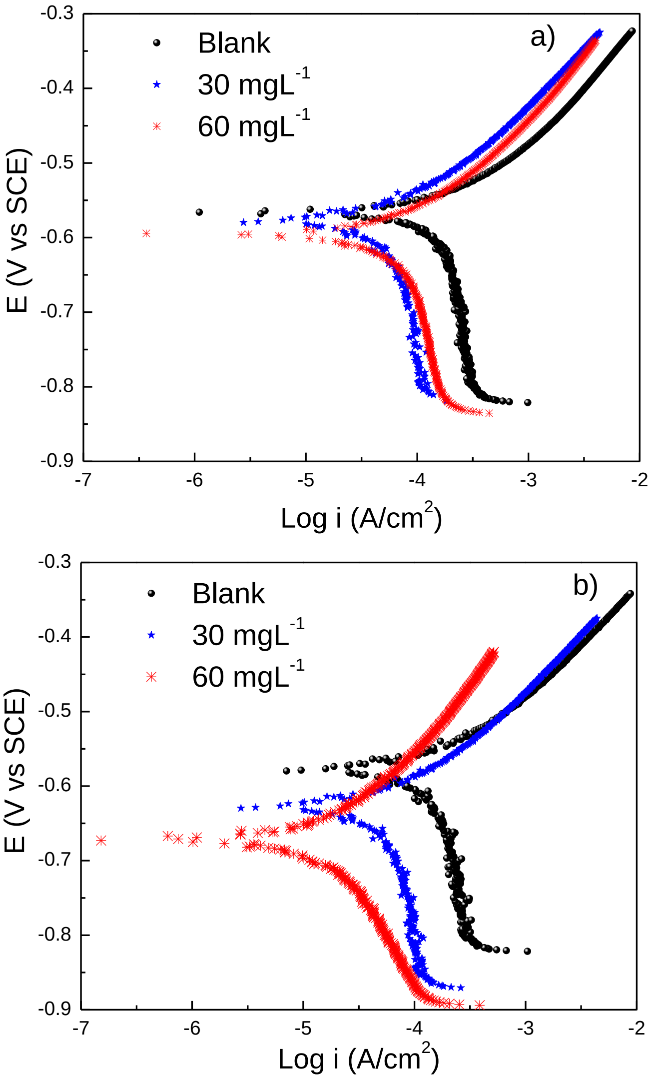


Figure 5. Polarization curves for X52 steel exposed to 2.45 wt% NaCl solutions for the blank and adding 30 and 60 mgL-1 of surfactant. a) OCP and b) -700 mV OFF.

Table 3. Electrochemical parameters derived from polarization curves of X52 steel in 2.45 wt% NaCl solutions adding Non-ionic NPE-4 surfactant dosage at 600 rpm, 1h and 30°C.

System		-E$_{corr}$ (mV/SCE)	i$_{corr}$ (A cm^{-2})	β$_a$ (V dec^{-1})	−β$_c$ (V dec^{-1})	CR (mm/year)
OCP	Blank	0.566	1.708 x10^{-4}	0.113	0.750	0.1980
	30 mgL^{-1}	0.579	1.591 x 10^{-4}	0.112	0.467	0.1844
	60 mgL^{-1}	0.594	1.3983 x 10^{-4}	0.110	0.470	0.1621
-700 mV	Blank	0.594	7.7985 x 10^{-5}	0.134	0.645	0.0904
	30 mgL^{-1}	0.629	4.658 x 10^{-5}	0.119	0.500	0.0510
	60 mgL^{-1}	0.672	1.0953 x 10^{-5}	0.118	0.137	0.0127

3.3. Adsorption process

The degree of surface coverage of the actives sites (θ) and the adsorption equilibrium constant (k_{ads}) of the metallic surface was calculated by the equations 3 to 5, that is associated with adsorption isotherms of Langmuir, Frumkin, Freundlich and Temkin [5, 6]. K_{ads} is directly related to the standard free energy of adsorption reaction ($\Delta G°_{ads}$) by the equation 6. The concentration surfactant ($C_{surfactant}$), θ, and the thermodynamic parameters calculated are given in Table 4.

$$\theta = \left[\frac{i_{corr.blank} - i_{corr.surfactant}}{i_{corr.blank}}\right] = \left[\frac{CR_{blank} - CR_{surfactant}}{CR_{blank}}\right] \tag{3}$$

$$\frac{C_{surfactant}}{\theta} = \frac{1}{k_{ads}} + C_{surfactant} \tag{4}$$

$$k_{ads} = \frac{1}{C_{surfactant}\left(\frac{1}{\theta} - 1\right)} \tag{5}$$

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 k_{ads}) \tag{6}$$

Table 4. Adsorption constants and thermodynamic parameters of Non-ionic NPE-4 surfactant dosage in 2.45 wt% NaCl solutions on X52 pipeline steel at 600 rpm, 1h and 30°C.

C$_{surfactant}$ (M)	Condition	θ	ln (55.5k$_{ads}$)	-ΔG°$_{ads}$ (kJ/mol)
0.0775	OCP	0.0243	2.8825	7.14
	-700 mV OFF	0.4358	5.5133	15.64
0.1550	OCP	0.1813	4.3729	10.83
	-700 mV OFF	0.8595	7.6917	19.05

Molecular weight of NPE-4 = 387 g/mol

The adsorption constant k_{ads} and $-\Delta G°_{ads}$ of X52 pipeline steel in the presence of surfactant in NaCl and 700 mV OFF displayed a higher value than OCP, which means that surfactant, is more easily adsorbed on X52 pipeline steel cathodically charged and as a result it provides a higher corrosion inhibition. It is well known that a negative value of $\Delta G°_{ads}$ indicate that adsorption occurred spontaneously with the formation of a film strongly adsorbed on the metal surface [5, 6]. Furthermore, $\Delta G°_{ads}$ around -20 kJ/mol or lower is associated with electrostatic interactions between the charged molecules and the charged metal, which indicates that a process of physical adsorption may occur [23, 25]. In this manner, 60 mgL^{-1} (0.1550 M) surfactant evaluated at -700 mV OFF exhibited a physical adsorption process. However, the lowest standard free energy belongs to 30 mgL^{-1} (0.0775 M) and OCP which means that surfactant is more difficult to adsorb on X52 steel surface and consequently it provides a little adsorption.

3.4. Surface finish after electrochemical test

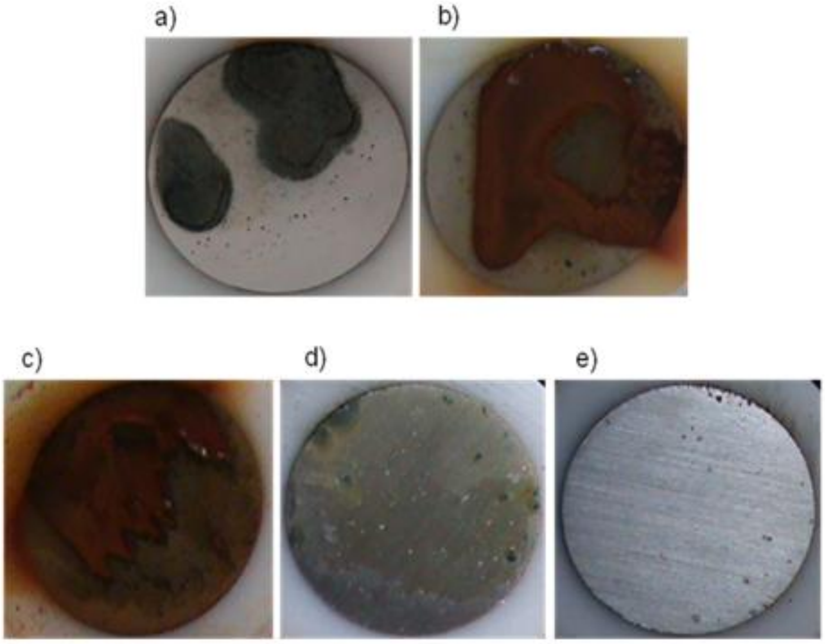


Figure 6. Surface finish of X52 steel after has been exposed to 2.45 wt% NaCl solutions in absence and presence of Non-ionic NPE-4 surfactant at 1h and 30°C. a) blank, OCP and 0 rpm, b) blank, OCP and 600 rpm, c) 30 mgL^{-1}, OCP and 600 rpm, d) 30 mgL^{-1}, 600 rpm and -700 mV OFF and e) 60 mgL^{-1}, 600 rpm and -700 mV OFF.

Fig. 6 shows some images of the visual analysis of the corrosion damage and inhibition effect on X52 steel after electrochemical tests; suggesting that the X52 steel in contact with 2.45 wt% NaCl solution exhibits different types of corrosion damage. Pitting and two dark areas on steel surface were observed on X52 steel at 0 rpm and OCP (Fig. 6a); while a greater oxidation and rust (iron oxides) was observed in presence of agitation as is observed in Fig. 6b. In addition, iron oxide production was accelerated with 30 mgL^{-1} surfactant and 600 rpm (Fig. 6c). In case of Fig. 6b and c, there was evidence of metal dissolution underneath the corrosion products. This dissolution process could possibly be involved in the depressed loop and the inductive effect observed at intermediate and low frequencies from Fig. 3a. In addition, an organic deposit and absence of rust were observed with the presence of -700 mV at the same dosage and stirring (Fig. 6d). However, adding 60 mgL^{-1} of surfactant and stirring at 600 rpm and -700 mV help to remain practically free of corrosion products as is shown in Fig. 6e.

4. CONCLUSIONS

The X52 pipeline steel in contact with chloride solution exhibits various types of corrosion damage using different hydrodynamic conditions, negative potential and different surfactant concentration. Low resistance values suggest the formation of corrosion products with non-protective properties. Non-ionic NPE-4 surfactant is a molecule that could be used as corrosion inhibitor of X52 steel exposed in chloride solutions. EIS and polarization curves analyses show a reasonable corrosion protection of X52 steel when surfactant concentration is increased from 30 to 60 mgL^{-1} in NaCl solution. The surfactant molecule affects the cathodic reaction; therefore it is classified as cathodic type inhibitor. However, thermodynamic parameters corroborate the modification of the protective properties of the surfactant. The standard free energy calculated was lower than -20 kJ/mol which indicates that a physical adsorption may occur and is associated with little adsorption.

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