Effect of Inhibitors based Amine Derivates on Some Carbon Steel Corrosion

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The purpose of this paper is to evaluate the variation of the corrosion rate of the AISI 316L and OL-37 alloys in reservoir waters and the analysis of these waters. Corrosion experiments were performed on two alloys samples, with and without corrosion inhibitors based on amino structures. Analyses were performed on a Princeton Applied Research potentiostat-galvanostat VSP, at room temperature and kinetic parameters of the corrosion were evaluated from the extrapolation of Tafel curves. According to the conventional scale for appreciating the corrosion resistance based on the corrosion rate determined by electrochemical metods, the OL-37 steel belongs to the resistance class-stable and to the stability group 2, and the AISI 316 L stainless steel belongs to the resistance class-very stable and to the stability group 2.The AISI 316L stainless steel is recommended to be used for the construction of fluid transporting pipelines from wells.

Key words: corrosion rate, reservoir waters, stainless steel, corrosion inhibitors

Corrosion is the deterioration of a *metal* as a result of chemical reactions between it and the surrounding environment. Any corrosion phenomenon fundamental approach must consider three factors: metal, metal interface / environment and environment. The oil industry is one of the main sectors where corrosion raises special problems, both in terms of economic operation of the installation, and security [1]. Steel is used very often in different fields due to its excellent thermal and electrical properties. The choice of corrosion resistant steels in the production of oil and gas pipelines is a complex procedure [2-5]. The most important water reservoir parameters that lead to the correct choice of steels are: the amount of salts (Cl^-), CO_2, $Ca^{2+,}$ S^{2-}(total) acidity and corrosive environment [6-8]. The action mode of dissolved salts in water is multiple: first, salts increase the conductivity of the water, due to their ionizing effect, thus enabling intensification of electrochemical corrosion phenomena. Sodium and potassium chlorides produce no difficulties because they do not hydrolyze, in contrast with HCl that is released as result of hydrolysis at temperatures above 120°C causes significant damage. There are many methods of corrosion control, but the most common is the use of corrosion inhibitors. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with media. The corrosion inhibition potential of many organic compounds was investigated. However, unfortunately, most of these compounds are not only expensive but also toxic to living beings. Therefore, many alternative eco-friendly corrosion inhibitors have been developed in recent days [6-14].

Different techniques can be used to assess the aspects of materials and conditions of a given electrochemical system. They can be classified according to the nature of their electrical signal as DC (direct current) and AC (alternate current) techniques. DC methods are the most often used in laboratory for the simplicity in use and data interpretation. They involve an application of either current or voltage with respective measurement of voltage or current. Examples of DC methods are Polarization Corrosion, Potentiostatic Polarization, Linear Polarization Resistance (LPR) and Potentiodynamic Porarization. The AC techniques measure the same variables, but they must be considered in a period. The data analysis is typically processed in a frequency domain. Examples of AC techniques are Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise [15].

Experimental part

Materials and methods

The corrosion inhibitors were prepared from the following materials: AMIX 1000 (from Basf), formaldehyde- FA 30% (from Momentive), olein (Interquim product) , hydrochloric acid and diethanolamine-DEA (Sigma-Aldrigh products).

The materials used in this study were made of steel, whose chemical composition is shown in table 1. Before each experiment, the alloy samples with a cylindrical shape were mechanically polished with a series of emery papers of 600, 1000 and 1500 grade, degreased in acetone, washed with sterile distilled water and dried.

The reservoir waters were collected from two points of drilling hole (water X and waterY) and the chemical composition is presented in table 2.

Table 1
CHEMICAL COMPOSITION OF THE ALLOYS

Samples	Composition, %							
AISI 316 L	C	Si	Mn	P	S	Cr	Mo	Ni	Others
	0.030	0.75	2.00	0.045	0.030	16.0/18.0	2.00/3.00	10.0/14.0	0.10
OL-37	Fe	C	Si	Mn	P	S	Al		
	98.293	0.150	0.090	0.400	0.023	0.620	0.022		

Table 2
RESERVOIR WATERS COMPOSITION

Proba	pH	S^{2-} (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	Ca^{2+} (mg/l)	CCOCr (mg/l)	Fe^{2+} (mg/l)	DT (^{0}H)
Water X	5,7	0,4	227	329,2	138	102,7	72,9	19.32
Water Y	6,2	0,4	232,6	327,5	142	75,5	0,17	19.6

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Corrosion measurements were performed with a VSP potentiostat at room temperature. The working electrode was prepared from a cylindrical sample, a Saturated Calomel Electrode (Hg/Hg_2Cl_2) as reference electrode and a carbon electrode as auxiliary electrode.

Preparations and characterizations of inhibitors

A three-necked flask equipped with a stirrer, thermometer and descending condenser was used for the preparation of the two inhibitors.

AMIX and diethanolamine were mixed in the round-bottom flask, in a weight ratio of 1:3. Formaldehyde was added at 30^0 C, slowly with stirring, at a molar ratio FA / DEA of 0.5 / 1 for variant A and 0.63 / 1 for variant B. This mixture was left for 6 h to condensate. In the second stage, was added olein and the mixture was heated to 160^0 C until the water of reaction is completely removed. The aminic nitrogen content of the two corrosion inhibitors prepared is shown in table 3.

Table 3
AMINO NITROGEN CONTENT OF THE INHIBITOR

Inhibitor	**% N**
Inhibitor A	1,13
Inhibitor B	1,28

Results and discussions

All electrochemical tests were carried out in a conventional three electrode corrosion cell. Potentiostatic polarisation curves were obtained with a scan rate of 2 mV/s and the potential range of -10V to +10V relative to the open circuit potential. The corrosion current density values were obtained by Tafel extrapolation method.

Table 4
RESERVOIR WATER X WITH AISI 316L

Inhibitor A (ppm)	**Ecorr (mV)**	**Icorr (µA)**	**βc (mV)**	**βa (mV)**	**Rp (Ohm)**
0	-734.960	8.397	215.6	333.8	6816.18
100 (ppm)	-580.888	1.939	245.1	424.7	32548.1
200 (ppm)	-449.528	1.862	248.3	440.2	37115.3
400 (ppm)	-403.749	1.675	278.8	414.6	40667.3
Inhibitor B (ppm)	**Ecorr (mV)**	**Icorr (µA)**	**βc (mV)**	**βa (mV)**	**Rp (Ohm**
100 (ppm)	-448.674	3.101	249.9	1085.1	22665.6
200 (ppm)	-388.118	3.291	230.3	1104.5	19760.2
400 (ppm)	-382.491	2.384	222.9	2689.6	25890.9

For the experimental research, two alloys were chosen and tested in waters reservoir with and without corrosion inhibitors. The corrosion inhibitors have an amino structure and the concentrations used were the following: 0, 100, 200 and 400 ppm. The kinetics parameters have been generated by EC-LAB software based on the following formula:

$$R_p = \frac{\Delta E}{\Delta i} = \frac{\beta_A \cdot \beta_C}{2{,}3 \cdot i_{cor} \cdot (\beta_A + \beta_C)} \qquad (1)$$

where:

- R_p is polarization resistance (a parabolic regression that is performed on the curve around the zero current potential ;

- β_A and β_C are the slope of the tangent to the anodic and cathodic branch of the curve;

-i_{cor} is the corrosion current measured in µA.

Polarization resistance is determined as the slope of the tangent to this parabola at the zero current potential.

The data for the AISI 316L alloy are structured in tables 4 and 5.

From the study of the anodic and the cathodic polarization curves (fig. 2, fig. 3) and comparing the parameters of corrosion (table 4), several aspects have been observed. Thus, in the concentration range of 0-100 ppm, corrosion rate decreases suddenly for both inhibitors and in the concentration range of 100-400 ppm, corrosion inhibitor B presents a better efficiency. Adding the inhibitor in the reservoir water leads to a reduction in the corrosion current density and thus a reduction of the corrosion rate of all three concentrations used.

From the figure 1 we can see that corrosion speed decreases with the increase of the inhibitor concentration. The corrosion inhibitor A has a better efficiency than the corrosion inhibitor B, as seen in figure 1. The best efficiency (70%) has the inhibitor A, at a concentration of 400 ppm, in the reservoir water X.

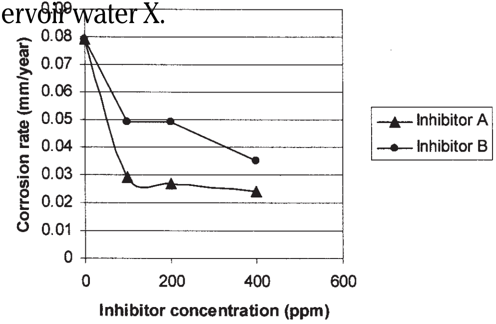


Fig. 1. Corrosion rate of AISI 316L in reservoir water type X as a function of the inhibitor concentration

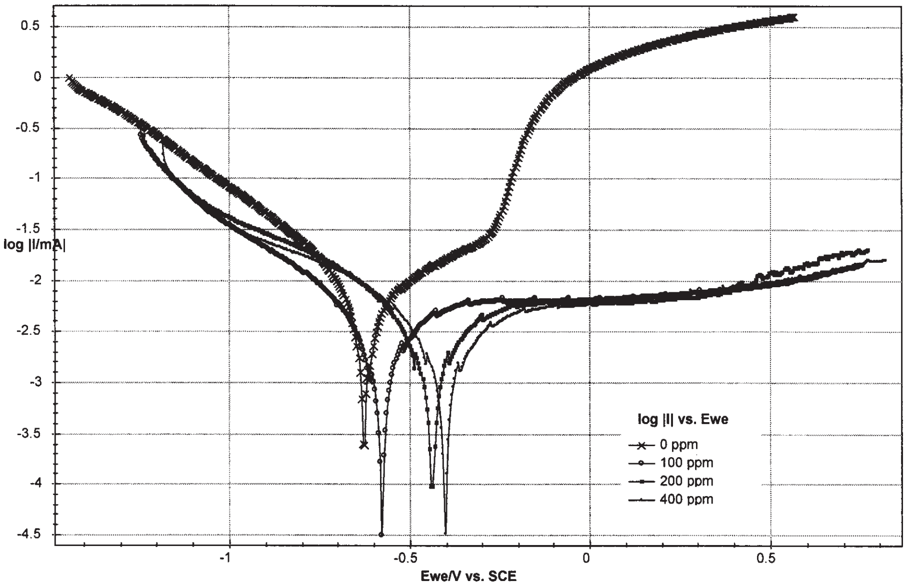


Fig. 2. Polarization curves for AISI 316L steel with and without the inhibitor A in reservoir water X

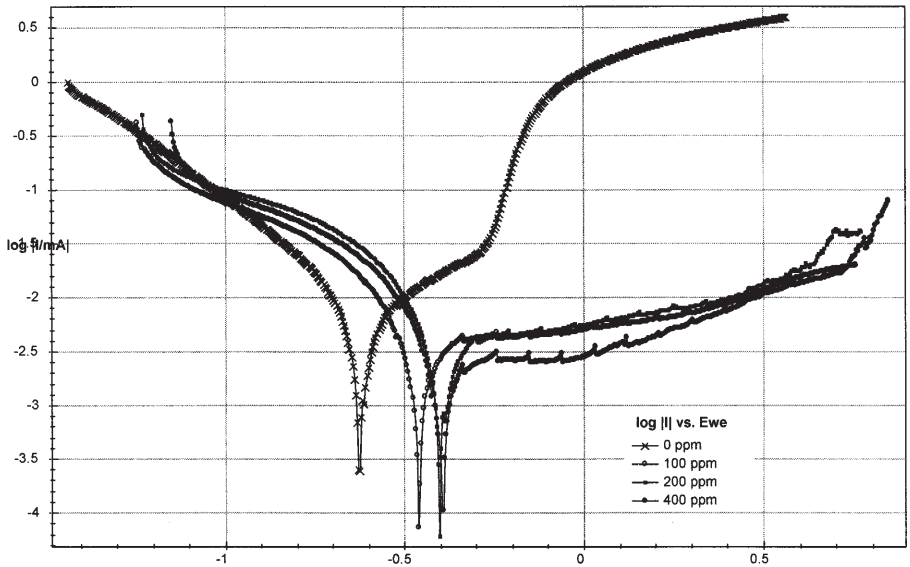


Fig. 3. Polarization curves for AISI 316L steel with and without inhibitor B in reservoir water X

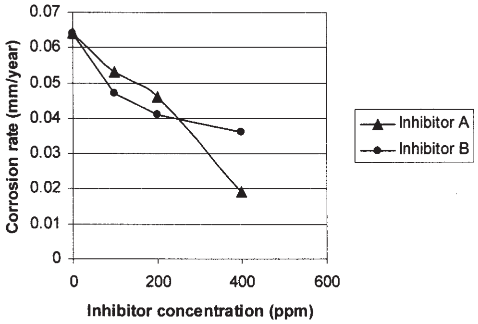


Fig. 4. Corrosion rate of AISI 316L in reservoir water Y as a function of the inhibitor concentration

Table 5

RESERVOIR WATER Y WITH AISI 316L

Inhibitor A (ppm)	Ecorr (mV)	Icorr (μA)	βc (mV)	Ba (mV)	Rp (Ohm)
0	-365,577	4,275	240,9	948,2	14185,6
100 (ppm)	-439,596	3,577	259,0	1088,5	20623,5
200 (ppm)	-433,476	3,100	252,9	87,4	22038,3
400 (ppm)	-332,635	1,308	194,6	1233,9	51176,3
Inhibitor B (ppm)	**Ecorr (mV)**	**Icorr (μA)**	**βc (mV)**	**βa (mV)**	**Rp (Ohm)**
100 (ppm)	-355,193	3,186	231,6	964,4	19704,4
200 (ppm)	-711.119	4.355	237.9	392.0	14395.0

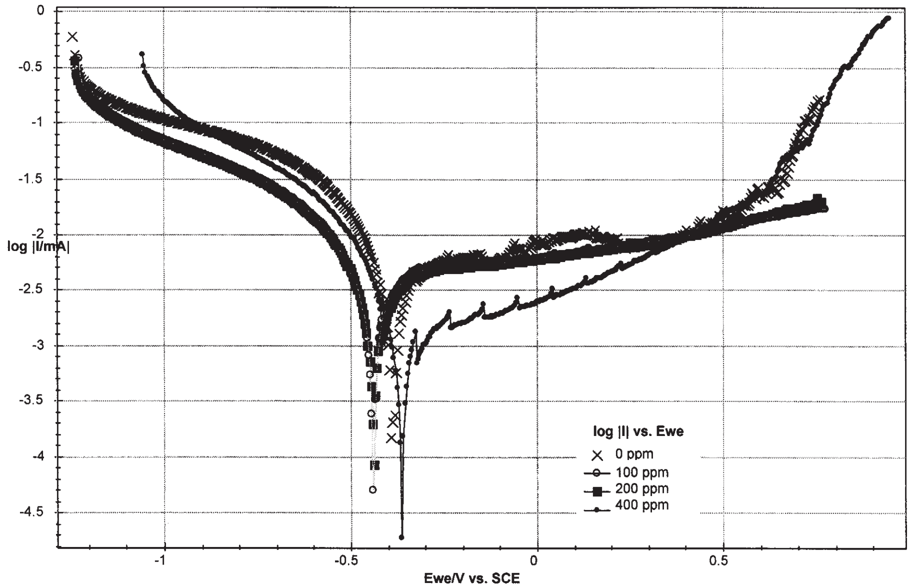


Fig 5. Polarization curves for AISI 316L steel with and without inhibitor A in reservoir water Y

From the study of the anodic and cathodic polarization curves (fig. 5, fig. 6), and from a comparison between parameters of corrosion shown in the table 5 several aspects have been observed. Thus, in reservoir water Y corrosion rates are comparable for the two inhibitors, with better efficiency for the inhibitor A. In the concentration range of 0-200 ppm, the inhibitor B has a better efficiency, and in the concentration range of 200-400 ppm the inhibitor A shows a better efficiency. Between 0-200 ppm, the inhibitor B has a better efficiency, but in the range of 200-400 ppm the inhibitor A shows a better efficiency.

From figure 4 one can see that the corrosion speed decreases with the increase of the inhibitor concentration, the best efficiency was obtained with the corrosion inhibitor A at a concentration of 400 ppm. Due to higher concentrations of salts and sulfur in the reservoir water X, the corrosion rate of steel AISI 316 is less than in the reservoir water Y, the corrosion rate decreasing from 0.079 mm / year to 0.064 mm / year.

The results of the tested materials in water reservoir X, for OL 37 steel are listed in table 6 and for water reservoir Y in table 7.

OL-37 steel has a higher corrosion rate in comparison with AISI 316L, in reservoir water X. The addition of inhibitors in water reservoir X (fig. 7) has increased the polarization resistance Rp, has decreased the current density and hence lowered i_{cor} and corrosion rate of the steel OL-37 for both

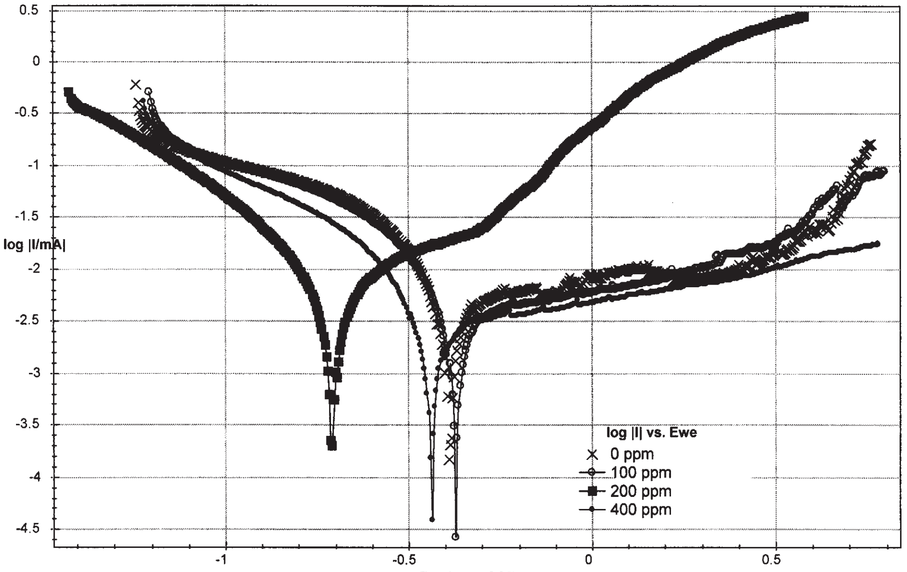


Fig. 6. Polarization curves for AISI 316L steel with and without inhibitory B in reservoir water Y

Table 6
RESERVOIR WATER TYPE X WITH OL-37 STEEL

Inhibitor A (ppm)	Ecorr (mV)	Icorr (μA)	βc (mV)	βa (mV)	Rp Ohm
0	-904.311	19.404	227.2	393.1	3114.89
100 (ppm)	-710.890	5.074	221.4	301.0	10670.60
200 (ppm)	-615.605	5.125	263.1	397.2	12084.40
400 (ppm)	-759.450	2.338	166.7	385.2	23976.60
Inhibitor B (ppm)	**Ecorr (mV)**	**Icorr (μA)**	**βc (mV)**	**Ba (mV)**	**Rp Ohm**
100 (ppm)	-665.444	5.575	270.1	424.4	11525.00
200 (ppm)	-804.746	3.573	181.1	383.5	17659.00
400 (ppm)	-603.050	2.132	287.9	227.5	26401.10

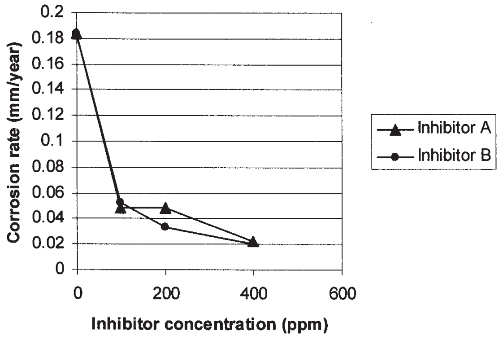


Fig. 7. The corrosion rate of OL-37 in reservoir water X as a function of the inhibitor concentration

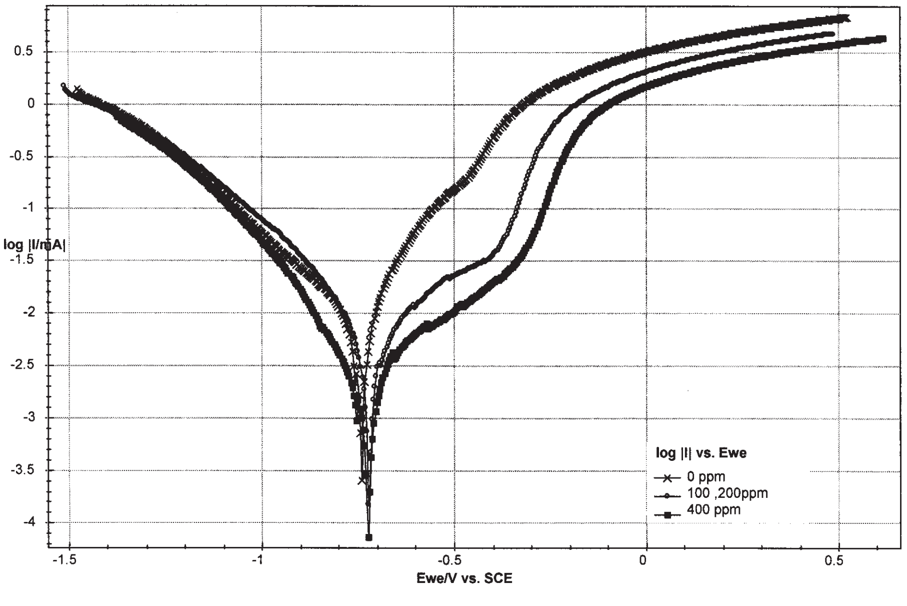


Fig. 8. Polarization curves for OL-37 steel with and without inhibitor A in reservoir water X

inhibitors (figs. 8, 9). The efficiency calculated for the two inhibitors is about 90% at a concentration of 400 ppm. In the concentration range of 0-100 ppm both inhibitors shows approximately equal efficiency, but in the concentration range of 100-400 ppm the inhibitor B shows better efficiency.

Analyzing the corrosion parameters and the Tafel curves from figures 10 and 11, we have found that the two inhibitors were relatively equal in efficiency, especially at the concentration of 400 ppm. The increase in concentration of the inhibitors A and B lead to the decrease of the corrosion rate. Thus, the efficiency calculated for the two inhibitors (table 8) is approximately 67%. In comparison with the corrosion rate of the alloy OL-37 in reservoir water X, the corrosion rate decreases in reservoir water Y(fig. 12).

If v_0 is denoted corrosion rate in the absence of inhibitor and v_i corrosion rate in the presence of inhibitor, P-corrosion protection that the inhibitor has the expression:

$$P = \frac{v_0 - v_i}{v_0} \cdot 100 \qquad (2)$$

where P is between 0 and 100.

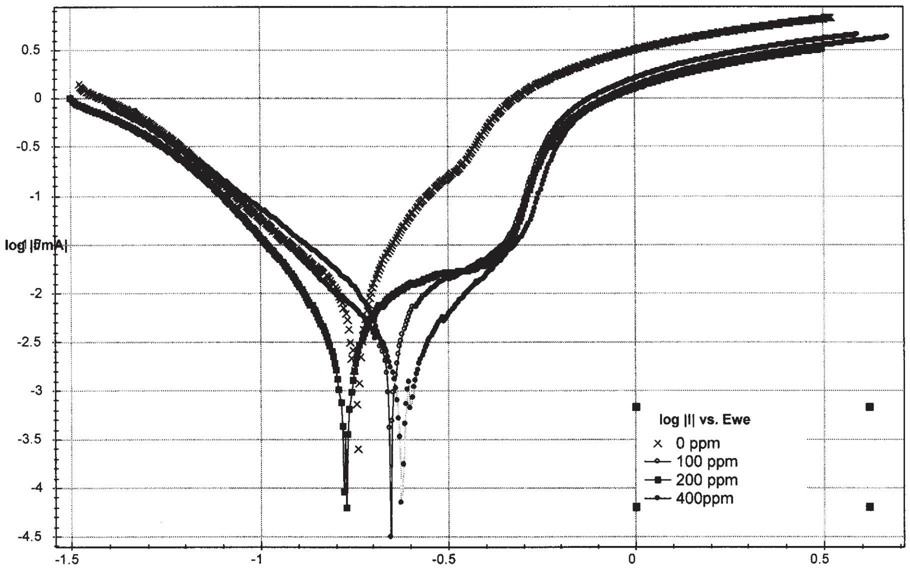


Fig. 9. Polarization curves for OL-37 steel with and without inhibitor B in reservoir water X

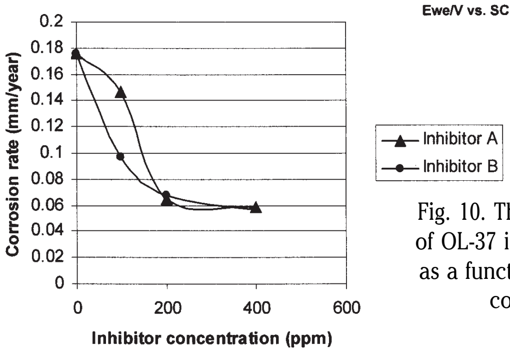


Fig. 10. The corrosion speed of OL-37 in reservoir water X as a function of the inhibitor concentration

Table 7

RESERVOIR WATER Y WITH OL-37

Inhibitor 1 (ppm)	Ecorr (mV)	Icorr (µA)	βc (mV)	βa (mV)	Rp (Ohm)
0	-689.392	18.544	467.2	165.9	2480.92
100 (ppm)	-956.925	15.360	191.6	540.3	3964.9
200 (ppm)	-602.916	6.910	274.0	324.7	8923.4
400 (ppm)	-781.477	6.204	200.9	369.2	9180.2
Inhibitor 2 (ppm)	**Ecorr (mV)**	**Icorr (µA)**	**Bc (mV)**	**Ba (mV)**	**Rp (Ohm)**
100 (ppm)	-875.361	10.294	186.4	375.8	5447.6
200 (ppm)	-741.892	7.227	249.4	388.7	8633.2
400 (ppm)	-689.892	6.065	301.3	315.4	10862.2

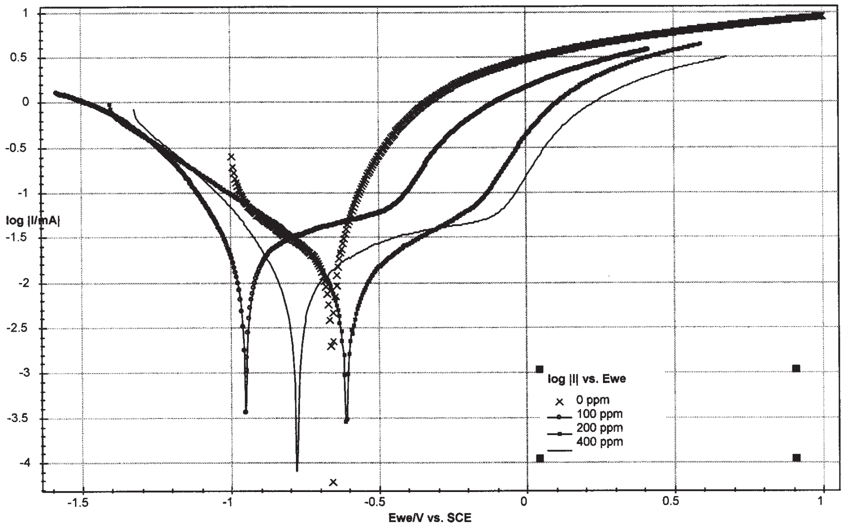


Fig. 11. Polarization curves for OL-37 steel with and without inhibitory A in reservoir water Y

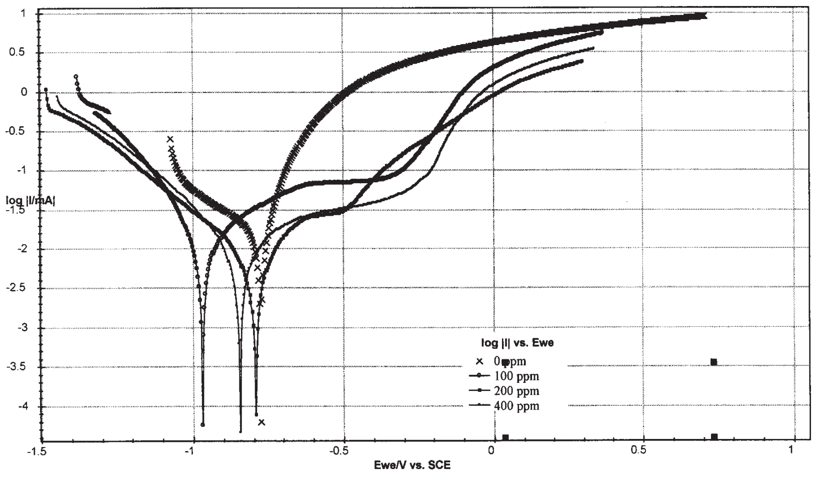
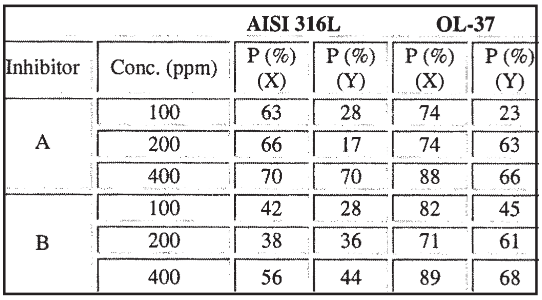


Fig. 12. Polarization curves for OL -37 steel with and without inhibitor B in reservoir water Y

Table 8
EFICIENCY OF CORROSION INHIBITORS BASED ON CONCENTRATION



		AISI 316L		OL-37	
Inhibitor	Conc. (ppm)	P (%) (X)	P (%) (Y)	P (%) (X)	P (%) (Y)
A	100	63	28	74	23
	200	66	17	74	63
	400	70	70	88	66
B	100	42	28	82	45
	200	38	36	71	61
	400	56	44	89	68

Conclusions

Experimental results carried out on the corrosion behaviour of two alloys upon contact with reservoir waters, lead to the following conclusions:

- two corrosion inhibitors were prepared by the condensation of a mixture of a fatty acid with amines followed by amidation, inhibitors which presented approximately equal efficiency for the three concentrations analyzed;
-for both corrosion inhibitors, the increase of concentratios lead to the decrease of corrosion rate;
- for the AISI 316L alloy, the inhibitor A had a maximum efficiency (70%) in both samples of reservoir water, at a concentration of 400 ppm;
- for OL37 steel, the inhibitor A had an efficiency of up to 88% in reservoir water X and no more than 66% in reservoir water Y, at a concentration of 400 ppm. For the same type of steel the inhibitor B had an efficiency of 89% in water X and of 68% in water Y, at an concentration of 400 ppm;
- OL37 steel had a corrosion rate much higher than the steel AISI 316L, thus it is not recommended for use in the construction of wells for oil extraction equipment;
- the corrosion inhibitors based on amino structures presented a good efficiency.

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Manuscreipt received: 20.11.2013