The Salts of Nitronic acid as CO_2-Corrosion Inhibitors

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ABSTRACT:

The salts of nitronic acids were obtained by nitration of higher olefins, both normal and isomeric structure in the presence of aqueous alkali. The resulting salts (Na^+, K^+, NH_4^+), were tested in CO_2 -media as a corrosion inhibitor. The results showed that, the protective effect of the linear nitronated olefins increases by increasing the number of carbon atoms. This is due to the fact that because of the branched structure of the compounds, it is much more difficult to form a dense protective layer on the metal surface. 20% solutions of nitronated ethanolamine in isopropyl alcohol was synthesized and tested as corrosion inhibitor in carbon dioxide environments. The results showed that diethanolamine nitron based on a mixture of normal olefins C_{16}-C_{18} at a concentration of 50 ppm has a high protective effect of 99.69%.

KEYWORDS: olefin; nitronic acid; corrosion inhibitors; carbon steel; CO_2-corrosion; nitronated olefins.
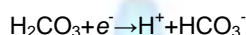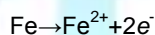
INTRODUCTION

In highly developed countries, solving the problem of corrosion protection in the oil and gas industry is of great importance. Because corrosion problems exist in the oil industry at every stage of production from the initial extraction to refining and storage prior to use, the application of corrosion inhibitors is required. When added a corrosion inhibitor in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. In the oil extraction and processing industries inhibitors often play an important role. They have always been considered to be the first line of defense against corrosion.

Oilfield corrosion manifests itself in several forms, among which are CO_2-corrosion and hydrogen sulfide corrosion in the produced fluids and corrosion by oxygen dissolved in water injection. These are by far the most prevalent forms of attack found in the oils and gas production [1-4].
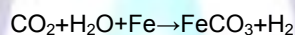
Because of an increased tendency to inject CO_2 into oil wells to reduce the viscosity of oil and increase the its production carbon dioxide (CO_2) corrosion of carbon steel pipelines and equipment in the oil and gas industry has been given much attention in recent years [5,6]. An important fact is that when CO_2 dissolves in water, carbonic acid (H_2CO_3) is produced with the characteristic that is more aggressive than hydrochloric acid at the same pH [7]. There are various mechanisms postulated for the CO_2 corrosion process but all involve either carbonic acid or the bicarbonate ion formed on dissolution of CO_2 in water. The best known mechanism was postulated by de Waard et al.[8] and was given as

$$H_2CO_3 + e^- \rightarrow H^+ + HCO_3^-$$

$$2H \rightarrow H_2$$

with steel reacting

$$Fe \rightarrow Fe^{2+} + 2e^-$$

overall

$$CO_2 + H_2O + Fe \rightarrow FeCO_3 + H_2$$

The presence of sulfur compounds in the oil and gas industries leads to increasing corrosion of equipment. In addition, at this stage, the main volume of oil extracted from oil reservoirs flooding waters is characterized by varying degrees of aggressiveness. In this case, the danger is contamination of reservoirs with sulfate-reducing bacteria. The purposeful use of various chemicals will solve several problems: inhibit corrosion, accelerate production, increase oil recovery, sterilize reservoirs, etc. Most corrosion inhibitors used in oilfields are organic compounds containing nitrogen or sulfur functionalities with a molecular structure which contains a polar head and a non-polar hydrocarbon chain having little attraction to water, called a hydrophobic tail [9-17].

To solve these problems, the development of highly effective corrosion inhibitors is of great scientific and practical. Note that in many oil fields due to their long-term operation in the extraction of liquid petroleum products, large quantities are contained under water. In such cases, the use of water soluble inhibitors is beneficial, because when feeding the inhibitor into the oil well it dissolves in formation water that goes along with the oil, reducing the corrosiveness of produced water. Upon further separation of water from oil and pumping into the reservoir along with corrosion protection, system download is provided by sterilizing the reservoir. Most water-soluble inhibitors are multifunctional, simultaneously stopping the vital activity of sulfate-reducing bacteria. Therefore the problem of water-soluble corrosion inhibitors must be addressed. Water-soluble inhibitors, depending on the chemical composition, are divided into 3 groups:

1) Complexes of alkyl amines and imidazolines with inorganic acids;

2) Water-soluble salts of alkyl arilsulfo acids;

3) Water-soluble salts of organic acids.

The reactants involved in all three groups have some flaws that complicate the work of the synthesis of water-soluble corrosion inhibitors based on them.

Given all of the above, we set a goal - the creation of multifunctional corrosion inhibitors on the basis of new chemical reagents. To do this, we saw fit to use organic nitronic acids. It should be noted that, prior to our studies, none was conducted in the world of research on the development of inhibitors on the basis of these chemical compounds. The theoretical sources of organic chemistry are to obtain salt by treatment with organic nitro compounds with alkalis, which exist only in solution.

MATERIAL AND METHODS

It is known that organic nitro compounds exist in two tautomeric forms, one of them is being nitronic acid:
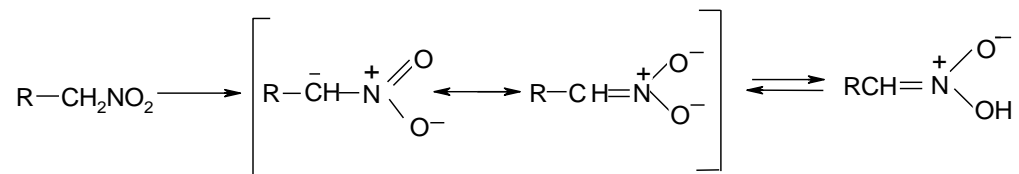
Thus, in free form, organic nitro compounds exist in the form of nitro compounds, as well as the nitronic acid. Therefore, in the processing of nitro compounds with alkalis, all nitro compounds are gradually transformed into the corresponding salts of nitronic acid. For salts of nitronic acid, we synthesized nitro compounds on the basis of 1-octene, 1-dodecene, 1-tetradecen, a mixture of α-olefins C_{16-18} from the oligomerization of ethylene, as well as trimers and tetramers of propylene and Na^+, K^+, NH_4^+ salts. The salts were used in 20% aqueous solutions of alkali. The reaction proceeds at room temperature. Some physicochemical properties of the 20% solutions of salts in isopropyl alcohol (IPA) are shown in Table 1.

Table 1: Physicochemical properties of the 20% solution of salts in isopropyl alcohol

№	Salts	Density, 20°C g /sm³	Refraction, n_D^{20}	Freezing temperature, °C
1	Nitronaty ammonium based on 1-octen	0.8749	1.3980	-60
2	Nitronaty ammonium based on 1-dodecene	0.8709	1.4010	-60
3	Nitronaty ammonium based on 1-tetradecene	0.8574	1.3980	-43
4	Nitronaty ammonium based on olefins C_{16-18}	0.7480	1.4030	-30
5	Nitronaty ammonium based on trimer of propylene	0.8874	1.3960	-60
6	Nitronaty ammonium based on tetramer of propylene	0.8624	1.3960	-60
7	Nitronaty potassium based on 1-octene	0.9309	1.3960	-60
8	Nitronaty potassium based on 1-dodecene	0.8952	1.3890	-50
9	Nitronaty potassium based on 1-tetradecene	0.8836	1.3900	-30
10	Nitronaty potassium based on olefins C_{16-18}	0.8813	1.3940	-35
11	Nitronaty potassium based on trimer of propylene	0.9276	1.3920	-56
12	Nitronaty potassium based on tetramer of propylene	0.7785	1.3920	-60
13	Nitronaty sodium based on 1-octene	0.8942	1.3920	-60
14	Nitronaty sodium based on 1-dodecene/	0.7875	1.4010	-50
15	Nitronaty sodium based on 1-tetradecene	0.8760	1.3950	-25
16	Nitronaty sodium based on olefins C_{16-18}	0.8563	1.3960	-15
17	Nitronaty sodium based on trimer of propylene	0.9035	1.3930	-60
18	Nitronaty sodium based on tetramer of propylene	1.0619	1.3920	-60

According to modern standard procedure, the effect of the obtained salts were studied on the corrosion of steel in the presence of an aqueous solution of NaCl, saturated with CO_2 [18, 19].

Chemical composition of carbon steel alloy

The rotating disk working electrodes for tests were made of carbon steel grade 080A15 with a surface area of 4.55 cm^2 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.

The test medium was 1% NaCl solutions saturated with carbon dioxide gas. 1% NaCl solution was prepared by dissolving analytical grade NaCl in distilled water. The concentration range of the prepared salts used for corrosion measurements was 50 ppm . All inhibitors solutions were prepared using distilled water.

Corrosion measurements

The measurements were performed on the rotating cylinder electrode (A=4.5cm^2). This electrode was used one time only. The reference electrode was an Ag/AgCl electrode to which all potentials are referred. Before beginning the experiment, the prepared 1% sodium chloride solution was stirred by a magnetic stirrer for 30 min in a 1000 ml cell. Then this cell was thermostated at 50 º 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 working electrode was formed oxide, the 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. An ACM Gill AC instrument connected to a personal computer was used for the measurements (Fig.1).

The percentage inhibition efficiency was calculated using the following formula [20].

$$\eta\% = \frac{\Delta Wu - \Delta Wi}{\Delta Wu} \times 100$$

where ΔWu and ΔWi are the weight loss of the metal in uninhibited acid and in inhibited solution respectively. The corrosion rate (CR) in mm/y can be calculated by the applying the 20% solution of salts at a concentration of 50 ppm produced the following results:

Table 2: Efficiency of corrosion protection of synthesized salts

| №	Salts	Inhibition efficiency, %
1.	Nitronaty ammonium based on 1-octen	17.8
2.	Nitronaty ammonium based on1-dodecene	97.08
3.	Nitronaty ammonium based on 1-tetradecene	97.03
4.	Nitronaty ammonium based on olefins C_{16-18}	99.2
5.	Nitronaty ammonium based on propylene trimer	stimulus
6.	Nitronaty ammonium based on propylene tetramer	9.48
7.	Nitronaty potassium based on 1-octene	46
8.	Nitronaty potassium based on 1-dodecene	98.52
9.	Nitronaty potassium based on 1-tetradecene	97.78
10.	Nitronaty potassium based on olefins C_{16-18}	99.74
11.	Nitronaty potassium based on propylene trimer	stimulus
12.	Nitronaty potassium based on propylene tetramer	25
13.	Nitronaty sodium based on 1-octene	3.7
14.	Nitronaty sodium based on 1-dodecene	99
15.	Nitronaty sodium based on 1-tetradecene	96
16.	Nitronaty sodium based on olefins C_{16-18}	99.9
17.	Nitronaty sodium based on propylene trimer	stimulus
18.	Nitronaty sodium based on propylene tetramer	stimulus
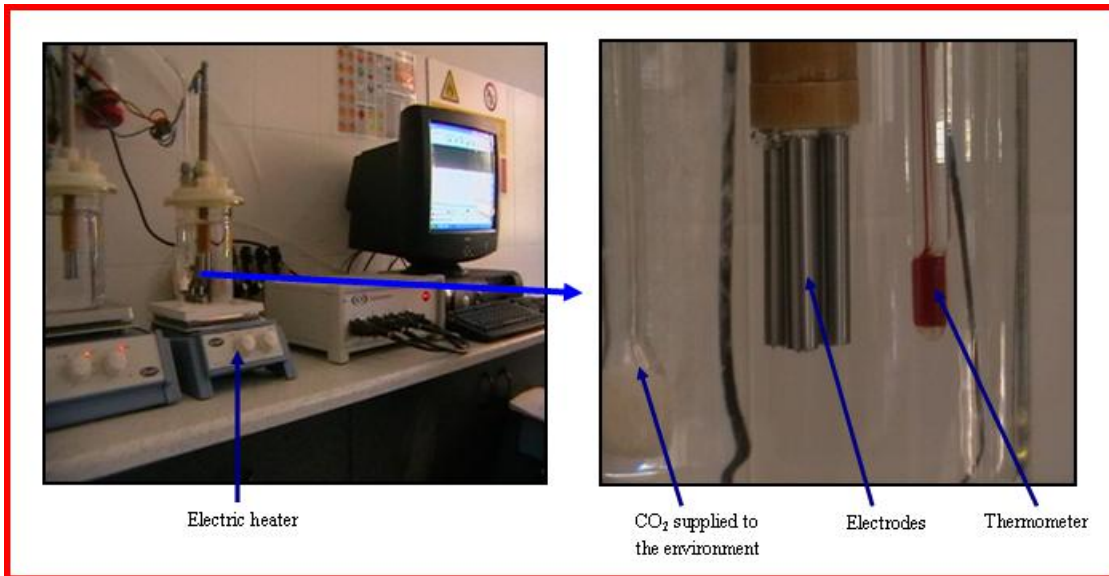
Figure 1: **General view of the apparatus ACM GILL AC**

The nitro compounds dissolved in the solutions prepared with inhibitors are conventionally called:

1) The nitro compound on the basis of 1-octene - T-1

2) Based on the nitro compound 1-dodecen- T-2

3) The nitro compound based on 1-tetradecen- T-3

4) The nitro compound from a mixture of α-olefins C_{16-18} - T-4

5) The nitro compound based on propylene trimer - T-5

6) Nitro compound based on propylene tetramer - T-6

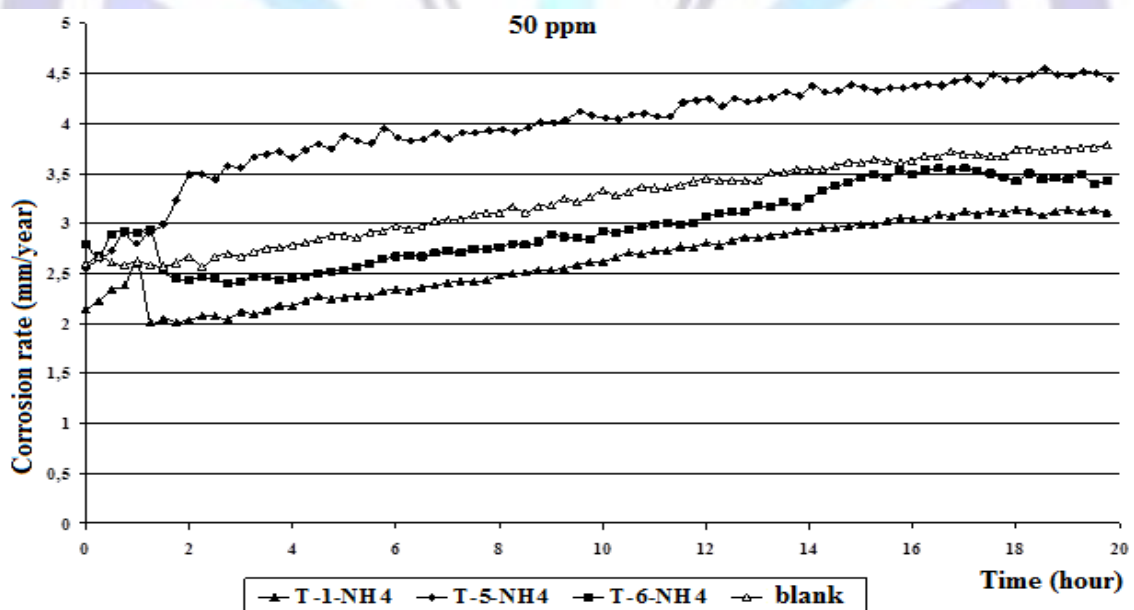The rates of corrosion of metals in pure vs. salt-inhibited media are shown in Figs. 2-7

Figure 2: The effect of ammonium salts on the basis nitronaty of 1-octene (T-1), propylene trimer (T-5) and tetramer (T-6) on the kinetics of corrosion of steel in CO_2-saturated brine at 50 ^{0}C.
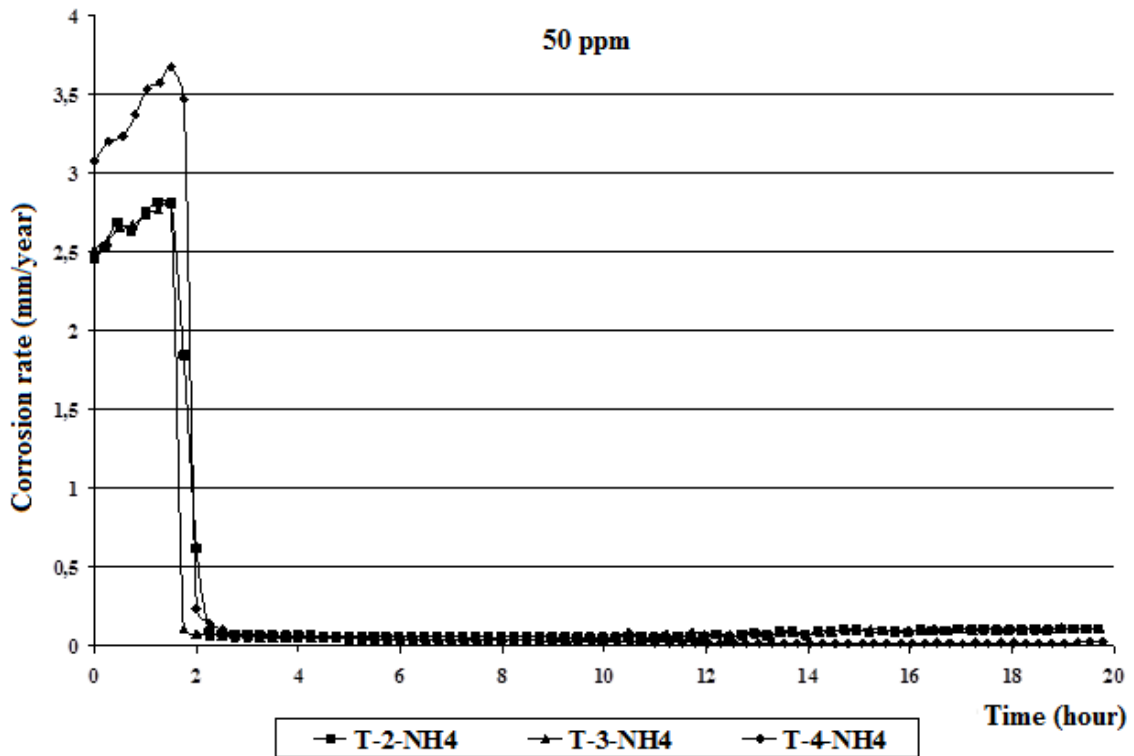
Figure 3: The effect of ammonium salts on the basis nitronaty of 1-dodecene (T-2), 1-tetradecene (T-3) and olefins C_{16}-C_{18} (T-4) on the kinetics of corrosion of steel in CO_2-saturated solution.
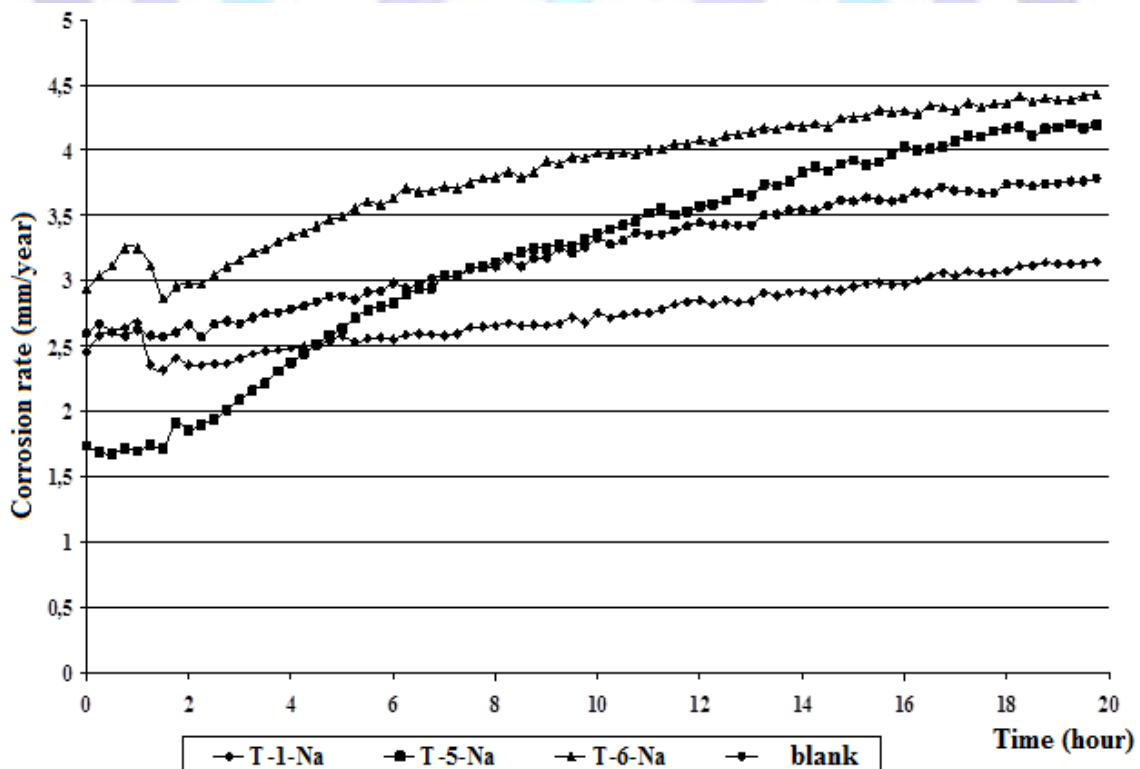

Figure 4: The effect of sodium salts based on nitronaty of 1-octene (T-1), propylene trimer (T-5) and tetramer (T-6) on the kinetics of corrosion of steel in CO_2-saturated brine at 50^0C
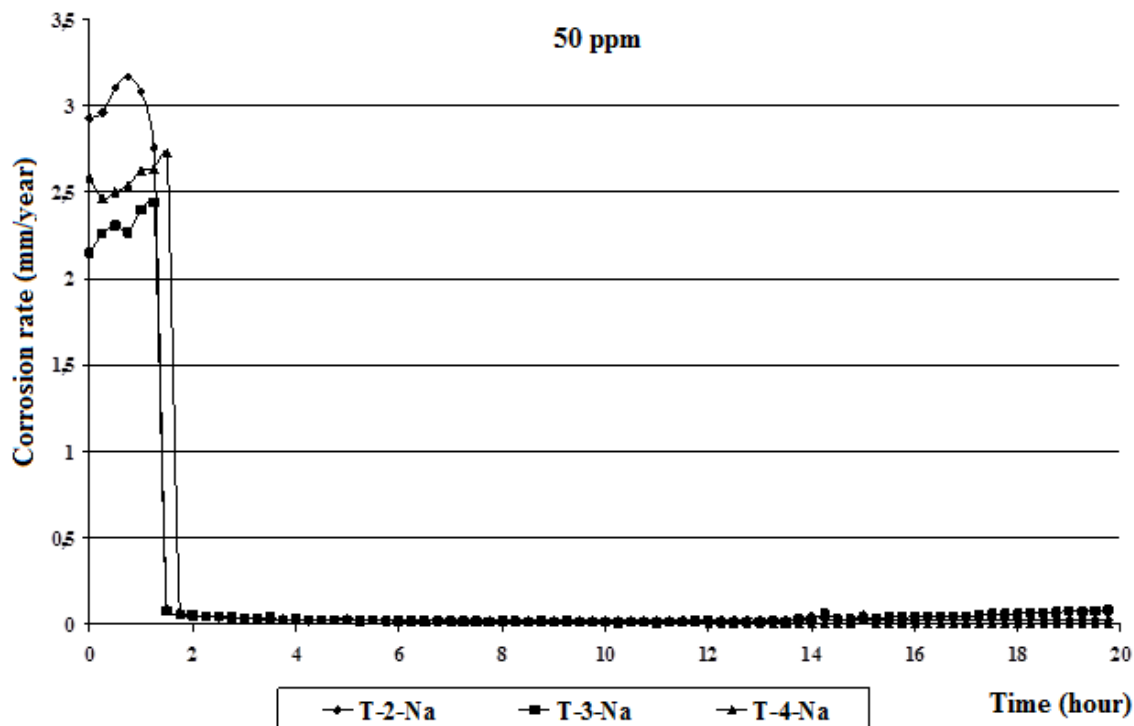
Figure 5: The effect of sodium salts on the basis nitronaty of 1-dodecene (T-2), tetradecene (T-3) and olefins C$_{16}$-C$_{18}$ (T-4) propylene on the kinetics of corrosion of steel in CO$_2$-saturated brine at 50 ^{0}C
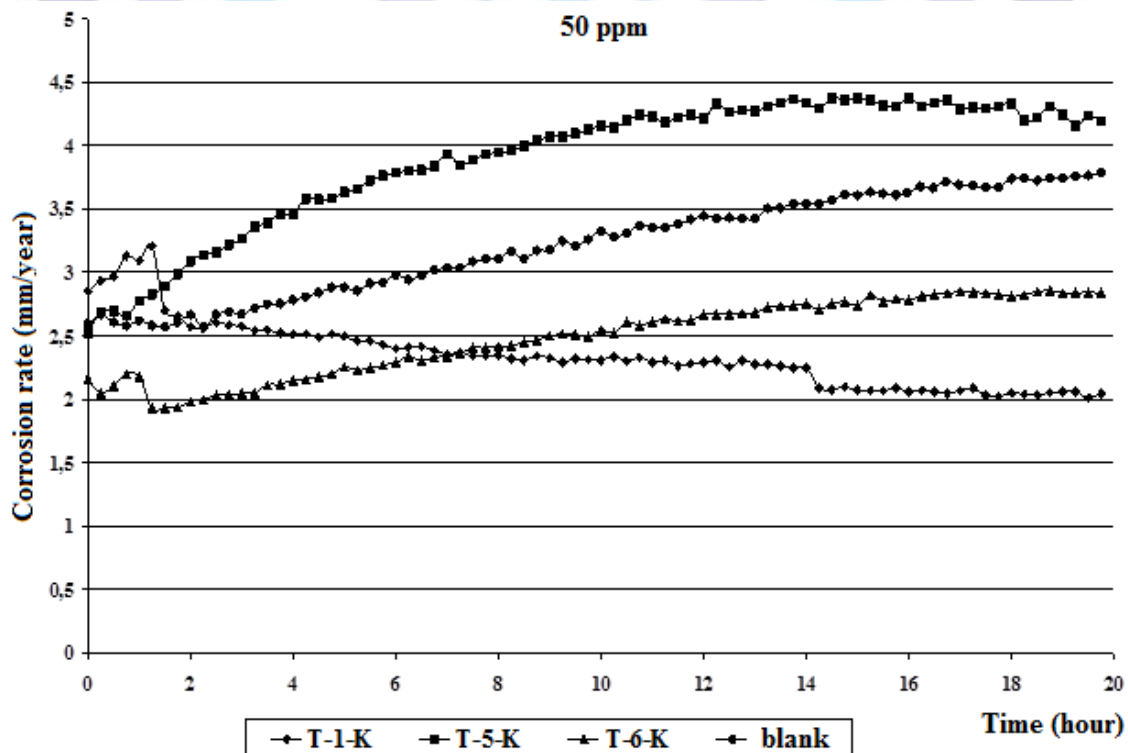

Figure 6: The effect of potassium salts on the basis nitronaty of 1-octene (T-1), propylene trimer (T-5) and tetramer(T-6) on the kinetics of corrosion of steel in CO$_2$-saturated brine at 50 °C
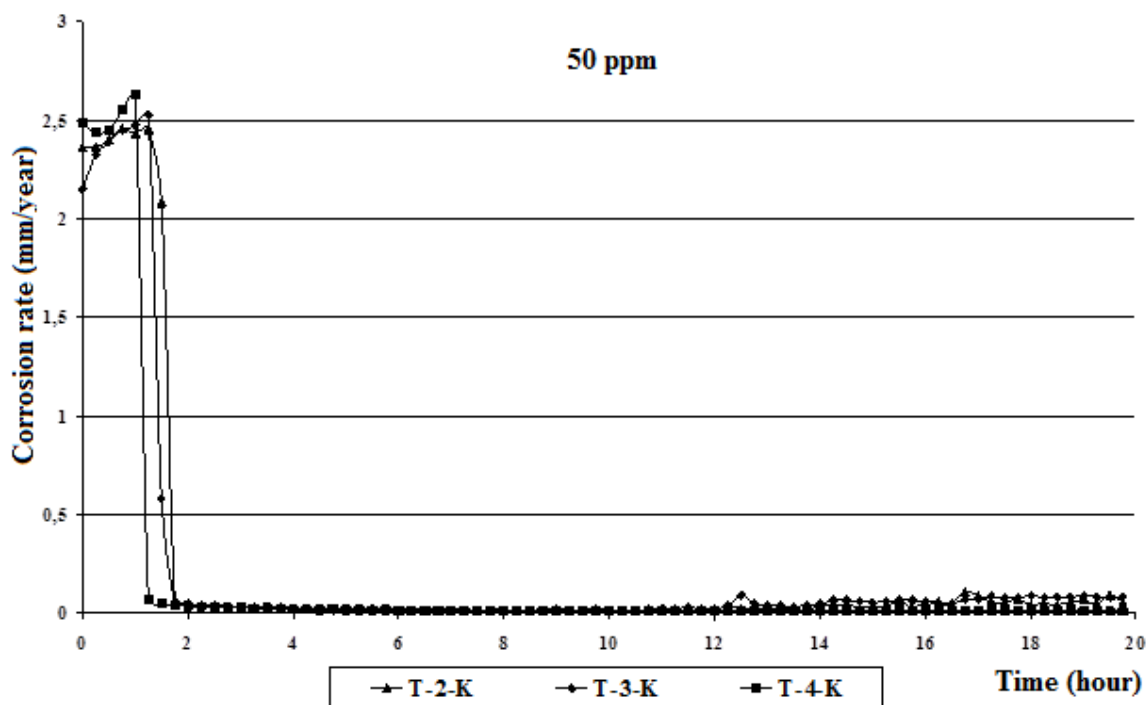
Figure 7: The effect of potassium salts on the basis nitronaty of 1-dodecene (T-2), tetradecene (T-3) and olefins C₁₆-C₁₈ (T-4) propylene on the kinetics of corrosion of steel in CO_2-saturated brine, temperature 50 ^{0}C

As can be seen from **Fig. 3,** nitronaty ammonium derived from a mixture of

α-olefins C_{16-18} has the highest protective ability against corrosion. These are the values of the protective effects of the following:

➢   Nitronated ammonium-based on 1-dodecen - 97.08%;

➢   Nitronated ammonium-based on 1-tetradecen - 97.03%;

➢   Nitronated ammonium in a mixture of α-olefins C_{16-18}-99.2%

The sodium salt of nitro compounds on the basis of 1-octene at a concentration of 50 ppm has almost no protective effect (3.7%). Sodium salt obtained on the basis of the propylene trimer and tetramer at the same concentration did not protect the steel, but rather stimulated the corrosion process. The results of the corrosion of steel in the sodium salts of nitro compounds derived from the 1- dodecene, 1- tetradecene and a mixture of α-olefins C_{16-18}, are shown in **Fig. 5.**

As can be seen from **Fig. 5**, the sodium salts of nitro compounds, derived from the dodecene-1, tetradecene-1 and a mixture of α-olefins C_{16-18} at a concentration of 50 ppm exhibit a high protective effect, respectively, 99, 96 and 99.9%. Nitronated sodium derived from a mixture of α-olefins C_{16-18} has the maximum protective ability against corrosion in this environment.

It is evident that nitronated potassium derived from propylene trimer stimulates the process of corrosion of steel, and potassium-based on nitronated 1-octene and propylene tetramer exhibit a slight protective effect against corrosion by only 46 and 25%, respectively (**Fig.6**).

Nitronated potassium-based on 1-dodecen, 1- tetradecen and a mixture of α-olefins C_{16-18} showed the following effects of corrosion protection:

1) Nitronated potassium-based on 1-dodecen - 98.52%;

2) On the basis of potassium nitronated 1- tetradecen- 97.78%;

3) Nitronated based on a mixture of potassium α-olefins C_{16-18} -99.74%.

Photos of the steel electrode after the experiments, before and after cleaning their surfaces, were made, using a forensic comparison microscope brand "Leica FS C" with a digital camera "Leica DC 490" and software "Leica İmage manager". With the help of a microscope photographs were taken of the electrodes, magnified at 4, 40, 80, 160 and 240. Here are a few photos of the electrodes taken under this microscope after the experiments.

Figure 8: Photo of the electrode, tested in a medium containing ammonium nitronaty based on propylene tetramer before washing at magnification 160 x

Figure 9: Photo of the electrode, tested in a medium containing ammonium nitronaty based on propylene tetramer after washing at magnification 160 x
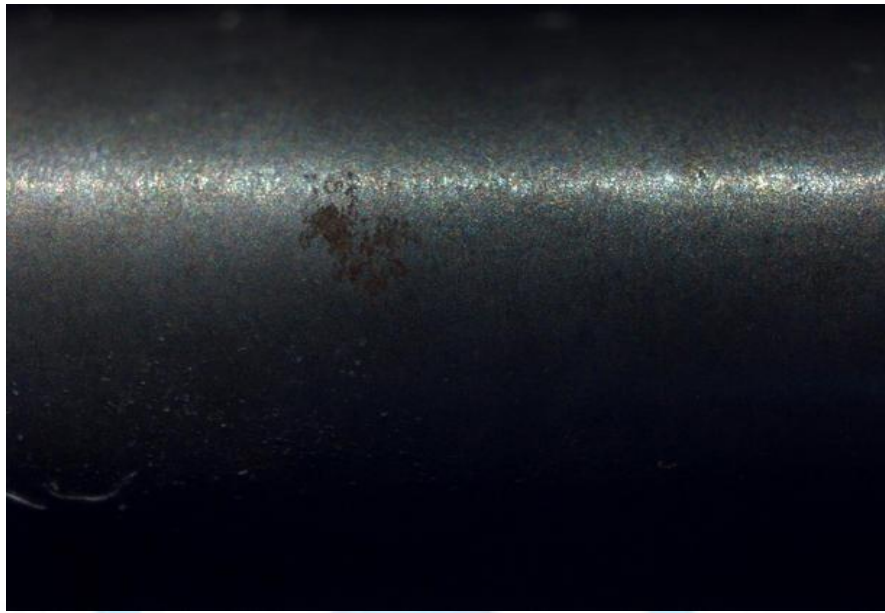
Figure 10: Photo of the electrode, tested in a medium containing sodium nitronaty based on 1-tetradecene before washing at magnification 80 x
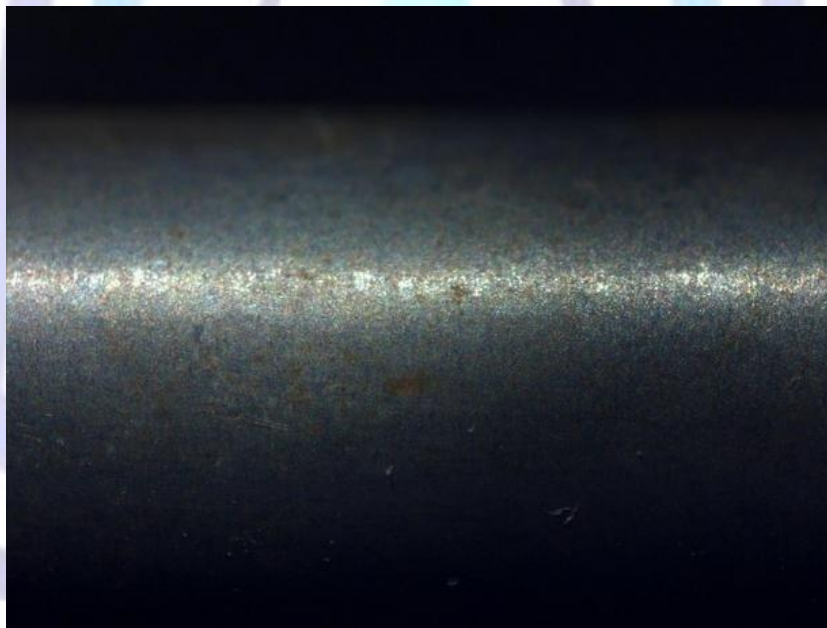

Figure 11: Photo of the electrode, tested in a medium containing sodium nitronaty based on 1-tetradecene after washing at magnification 80 x

The results show that the effect of salts of nitro compounds on the kinetics of the corrosion process of steel in a medium with 1% aqueous solution of NaCl, saturated with CO_2, depends on three factors:

1) The length of the alkyl radical;

2) The structure of the alkyl radical;

3) The type of cation.

As can be seen, with an increase in the radical of the C_8 to C_{16-18}, the effects change dramatically. This difference is most clearly manifested in the case of nitro compounds on the basis of octene-1. This further proves that one of the most important factors for a high protective effect of the inhibitor is the length of the radical, which creates the effect of screening. Studies also showed that the branching structure of the radical, dramatically reduced the protective effect. This

is due to the fact that the branched structure of the radical inhibitor molecule becomes intensive, and therefore cannot form a dense layer on the metal surface. Thus, it is advisable to use chemical compounds of normal structure as inhibitors. Another interesting results is the identification of the inhibitory effect of salt, depending on the nature of the cations. If the ammonium salt of nitronic acid octene-1 at a concentration of 50 ppm protects against corrosion by only 17.8%, the potassium and sodium salts of the same nitro compounds with the same concentration show a protective effect of 46% and 3.7%, respectively. Another interesting fact is that the ammonium, potassium and sodium salts of dodecene nitro-1-tetradecene, and a mixture of α-olefins C_{16-18}, with the same concentration show similar values, and the protective effect is in the range 97-99.74%. Apparently this is due to the rather large size and the normal structure of the radical in these salts, which dramatically increases the effect of adaptation of the formed protective layer.

Researched nitrony salts depending on their concentration, differently influence suppression of the rise of both sulfate-reducing bacteria (SRB). Nitronaty sodium, ammonium, potassium, derived from C_{12}, C_{14} and C_{16-18} at concentrations of 5 ppm can inhibit the growth of SRB.

All of these studies also indicate that when creating these types of inhibitors, bactericides, all three cations can be used and thus increases the selection of readily available raw materials.

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