Influence of Nitrite and Molybdate Blend on Carbon Steel Inhibition in Chloride Containing Solutions

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Abstract

Carbon steel inhibition has been managed by various methods of protection including cathodic protection, process control, reduction of the metal impurity content, and application of surface treatment techniques, as well as incorporation of suitable alloys. Inorganic and organic inhibitors are toxic and costly and thus recent focus has been turned to develop environmentally friendly inhibitors. Nitrites are now being increasingly used as environmental friendly inorganic corrosion inhibitor due to their low order of toxicity. Moreover, Nitrites are considered to be one of the most commonly used anodic inhibitors, shifting the corrosion potential to more noble values and consequently reducing corrosion. Molybdate based inhibitor has long been known as an inorganic and anodic type of corrosion inhibitor, which is effective for protecting mild steel. In order to achieve better efficiency and reduce the quantity of molybdate, we used a blend of nitrites and molybdates. In our work the experiments were conducted in the presence of $NaNO_2$ with different concentrations in order to achieve the best efficiency values. Among the range of $NaNO_2$ and Na_2MoO_4 concentrations used separately, at a lower concentration of 2 g/L efficiencies of 65% and 53% were achieved, respectively. However when molybdate was used as an additive, the blend at lower concentrations (2 g/L) resulted in 8.6 a synergism parameter, which indicates the synergistic effect of the mixture. The lower concentrations mixture of ratio 1:1 raised the efficiency to 93%.

Keywords: *synergistic effect of nitrites and molybdates.*

1. Introduction

It is known that corrosion is a natural process and is impossible to prevent completely. Thus we only try to control corrosion. Even though coatings and cathodic protection are often more effective, chemical inhibitors are also widely used to reduce corrosion particularly in oil and gas industry.

Among the various methods of protection, corrosion inhibitors are considered as one of the best know methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method [1-3]. Historically, inhibitors had great acceptance in the industries due to excellent anti-corrosive proprieties. However, many showed up as a secondary effect, damage the environment. Thus, the scientific community began searching for friendly environmentally inhibitors, like the organic inhibitors. Legault and Walker recorded the use of sodium nitrite ($NaNO_2$) as a corrosion inhibitor for mild [6]. They concluded that the function of nitrite is to maintain the oxide film formed on the metal's surface. $NaNO_2$ as an oxidizing inhibitor provides a thin film of products of electrochemical action as a passive surface on the metal.

Nitrite is considered to be one of the most commonly used anodic inhibitors, shifting the corrosion potential to more noble values and reducing corrosion rates [7]. At low concentrations of $NaNO_2$, the nitrite may create imperfect passivity and subsequently the corrosion will be increased. Molybdate inhibitors have long been known as an inorganic and anodic type of corrosion inhibitor, which is effective for protecting mild steel in the pH range 5.8–8.5 [8, 9]. Usually higher molybdate concentrations are necessary for corrosion inhibition that is economically unfavourable [10, 11].

2. Experimental work

2.1 Materials and Solutions:

2.1.1 Electrolytes:

All test solutions were prepared from analytical grade reagents and de-ionized water. The solutions that were used in the experimental work as following:

- 3.5% (35 g/L) of NaCl solution (blank solution).
- Different $NaNO_2$ concentrations (2, 4, 6, 8 and 10 g/L).
- Different Na_2MoO_4 concentrations (2, 4, 6, 8 and 10 g/L).
- 2 g $NaNO_2$ + Different Na_2MoO_4 concentrations (2, 4, 6, 8 and 10 g/L).

After the required weights of NaCl and $NaNO_2$ were determined using the digital balance. Beakers of 500 ml were used for all measurements and a magnetic stirrer was used for mixing the solutions.

2.1.2 Coupons (specimens)

The Coupons (specimens) were rectangular of 1018 carbon steel with the following dimensions (6 cm long, 1.2 cm width and 0.1 cm thick) as can be seen in Fig. 1 below. If only considered the surface that will be exposed to the test solution as a result the exposed area of 15.84 cm^2 (2.37 in^2) is considered.

Figure 1 Samples (coupons) that used in weight loss measurements

The composition and properties of the steel specimen are given below in table1.

Table 1 Carbon steel AISI 1018 composition

Element	Weight %
Carbon (C)	0.15-0.20
Manganese (Mn)	0.60-0.90
Phosphorous (P)	0.040 (max)
Sulfur (S)	0.050 (max)
Iron (Fe)	Remainder

2.1.3 Specimen preparation

A few specimens as shown in Figure 1 above were used throughout the weight loss measurements. The coupons surfaces were polished with SiC paper up to 1200 grit, washed with distilled water, degreased with acetone, and dried in air.

Apparatus and experimental arrangement Beakers of 500 ml capacity were used for the weight loss measurement. A digital balance with 4 digits as shown in Figure 2 was used to measure the weights of the samples prior and after the tests.

Figure 2 Digital balance used in weight loss measurements

Basically, a weight loss technique was used to calculate the corrosion rate of carbon steel specimens (samples) and to test the effect of sodium nitrate ($NaNO_2$) as inhibitor. Additionally sodium molybdate (Na_2MoO_4) was used alone and also as an additive to ($NaNO_2$) in order to check the synergistic effect of the blend. All measurements were run at room temperature 25 Cº (298 Kº).

2.3 Determination of corrosion rate using weight loss

Corrosion rate (CR) is calculated from the following formula:

$$CR = \frac{534\,(Wi - Wf)}{Atd}$$

Where;

CR = Corrosion rate (mpy)

W_i = Coupon initial weight (mg)

W_f = Coupon final weight (mg)

A = Surface area of the coupon (in^2)

T = exposure time (hrs.)

d = density of the alloy (g/cm^3)

2.4 Inhibitor efficiency (%)

The efficiency of an inhibitor can be calculated by the following formula:

$$\text{Inhibitor efficiency } (\%) = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}}$$

Where;

$CR_{uninhibited}$ = corrosion rate of the uninhibited system.

$CR_{inhibited}$ = corrosion rate of the inhibited system.

2.5 Synergism parameter (SI)

In order to calculate the effect of blending the two inhibitors, $NaNO_2$ and Na_2MoO_4, the synergism parameter to be calculated from the following formula:

Synergism parameter (S_1) $= \frac{1 - \theta 1{+}2}{1 - \theta' 1{+}2}$

The degree of surface coverage (θ) is calculated as following:

$$(\theta) = \frac{\text{CRuninhibited} - \text{CRinhibited}}{\text{CRuninhibited}}$$

Where;

$\theta 1 + 2 = (\theta 1 + \theta_2)\ (\theta_1 \times \theta_2)$

$\theta 1$ = surface coverage of inhibitor

θ_2 = surface coverage of additive

$\theta'1 + 2$ = the combined surface coverage of inhibitor and additive.

$S_1 > 1$ implies the existence of inhibition synergism between the two substances.

3. Results and discussions

3.1 Corrosion rate

In order to calculate the corrosion rate, the coupons were immersed in a blank solution for 168 hours (one week). Fig. 3 below illustrates the corrosion of samples in blank solution. The change can be noticed from the colour of the two beakers.

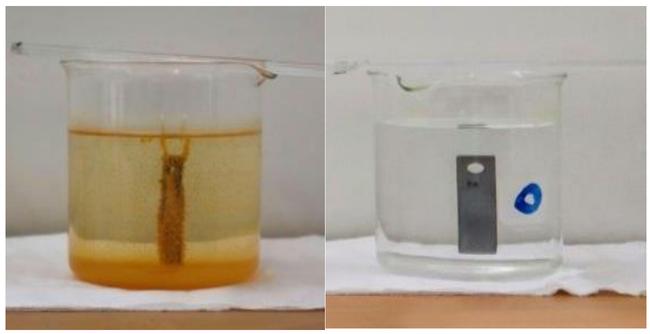

Figure 3 Coupons after the beginning of immersion and after 168 hrs. in a blank solution (from right to left)

The corrosion rate was measured three times (3 tests) and the results of these tests were in accordance as can be noticed from table 2 below.

Table 2 Corrosion rates of 3 tests

Test no.	Corrosion rate (mpy)
1	10.66
2	10.30
3	9.97

3.2. Effect of Sodium Nitrite Concentration

In order to examine the efficiency of the tested $NaNO_2$ as an inhibitor the coupons were immersed in blank and in different NaNO2 concentrations for a period of 168 hours. Fig. 4 clearly illustrates the immersed samples after 168 hours of immersion in 2, 4, 6, 8 and 10 g/L of $NaNO_2$ solutions.

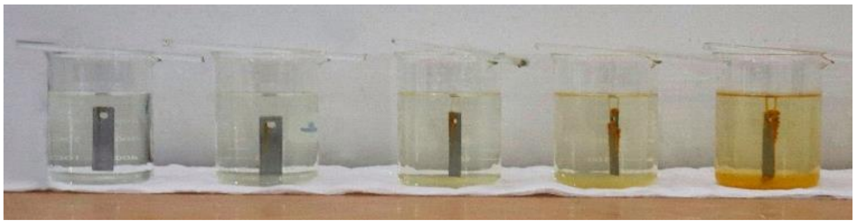

Figure 4 Coupons after 168 hrs. of immersion in 2, 4, 6, 8 and 10 g/L of $NaNO_2$ solutions (from right to left)

Corrosion rates and efficiencies of the tested coupons in a blank and in different concentrations of $NaNO_2$ are represented in table 3 below.

Table 3 Corrosion rates and the efficiencies in different $NaNO_2$ concentrations for 168 hrs.

Coupon no.	Concentration of $NaNO_2$ (g/L)	Corrosion rate (mpy)	Efficiency (%)
26	0	10.30	0
39	2	3.61	65
43	4	2.30	78
64	6	0.99	90
70	8	1.12	89
71	10	0.76	93

When using no inhibitor the corrosion rate was quite high (10.3 mpy) and when started using $NaNO_2$ as inhibitor the corrosion rate started to decrease with increase of $NaNO_2$ concentrations. Figure 5 below illustrates the corrosion rate vs. $NaNO_2$ concentration ranges used.

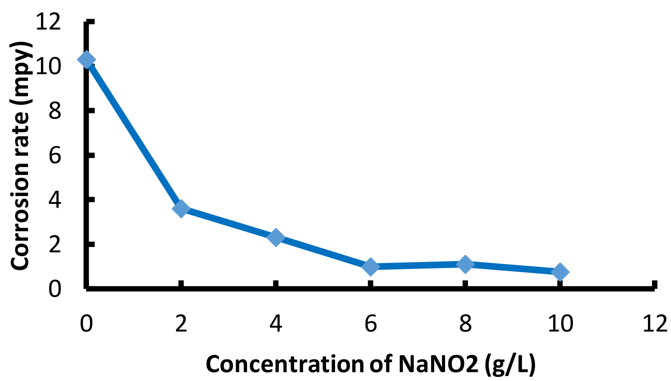

Figure 5 Corrosion rate vs. $NaNO_2$ concentrations

It is clear from figure 5 the corrosion rate was dropped from 10.3 to 3.61 and 2.30 mpy at concentrations of 2 and 4 g/L respectively. A very crucial drop to 0.99 mpy corresponding to 90% efficiency was achieved at 6 g/L and that was considered to be the optimum concentration among all concentrations used.

3.3. Effect of Sodium Molybdate Concentration

When used sodium Molybdate (Na_2MoNO_2) as an inhibitor with same concentration ranges as $NaNO_2$, the effect was not as good as nitrites. Figure 6 represents the immersed samples after 168 hours of immersion in 2, 4, 6, 8 and 10 g/L of Na_2MoNO_2 solutions.

Figure 6 Coupons after 168 hrs. of immersion in 2, 4, 6, 8 and 10 g/L of Na_2MoO_4 solutions (from right to left

The results of the effect of Na_2MoNO_2 as an inhibitor are tabulated below in table 4.

Table 4 Corrosion rates and the efficiencies in different Na_2MoO_2 concentrations for 168 hrs.

Coupon no.	Concentration of Na_2MoO_4 (g/L)	Corrosion rate (mpy)	Efficiency (%)
26	0	10.30	0
39	2	4.78	53
43	4	4.47	56
64	6	4.35	57
70	8	3.08	70
71	10	3.16	69

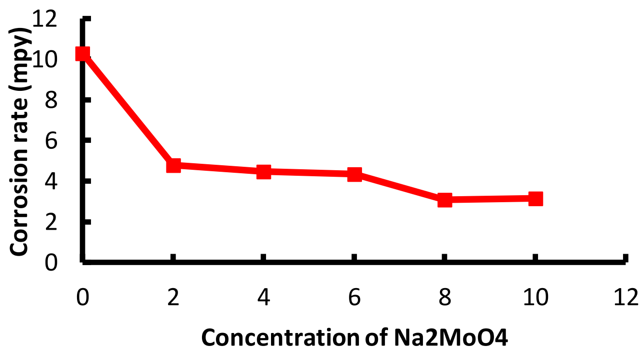

Figure 7 Corrosion rate vs. Na_2MoO_4 concentrations

3.4. Effect of Molybdate additives to Nitrite (blend)

In the last part of our work we proposed to evaluate the synergistic inhibition efficiency of sodium nitrite with sodium molybdate.

The synergistic effect of different concentration ranges (2, 4, 6, 8 and 10 g/L) of the Na_2MoO_4 additive to a fixed 2 g/L 0f $NaNO_2$ was studied. It is clear from figure 8 below that from the beakers (tests) at different concentrations the corrosion rate was quite negligible.

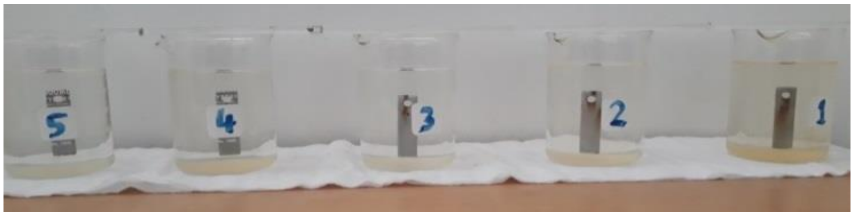

Figure 8 Coupons after 168 hrs. of immersion in 2 g/L of $NaNO_2$+2, 4, 6, 8 and 10 g/L of Na_2MoO_4 solutions (from right to left)

Table 5 Corrosion rates and efficiencies for different inhibitor blends

Coupon no.	Concentration of Na2MoO_4 (g/L)	Corrosion rate (mpy)	Efficiency (%)
26	0	10.30	0
39	2 g NaNO2 +2 g Na_2MoO_4	0.64	93
43	2 g $NaNO_2$ +4 g Na_2MoO_4	0.34	96
64	2 g $NaNO_2$ +6 g Na_2MoO_4	0.24	97
70	2 g $NaNO_2$ +8 g Na_2MoO_4	0.31	96
71	2 g $NaNO_2$ +10 g Na_2MoO_4	0.83	91

It can be noticed from table 5 that the blend of 2g/L $NaNO_2$ and 2g/L Na_2MoO_4 (1:1) ratio decreased the corrosion rate to a minimum value of 0.64 mpy compared to other values 3.61 and 4.78 when using nitrite and molybdate separately.

The effect of inhibitive action of sodium nitrite and sodium molybdate mixture on corrosion of mild steel in chloride medium is shown in Fig. 9. This indicates that better protection of the steel was obtained with the mixture of these reagents than with either of the inhibitors was used. It is clear that more protection is visible at lower concentration of the mixture of these inhibitors.

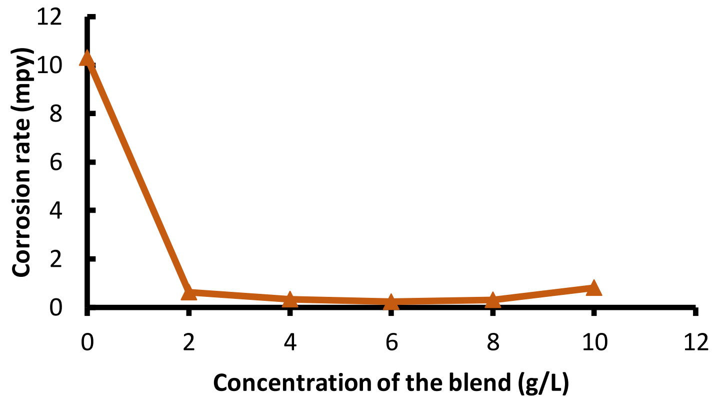

Figure 9 Corrosion rate vs. different Na_2MoO_4 concentrations+ 2 g/L $NaNO_2$

In fact, the decrease in corrosion rate and increase in efficiency were due to the coverage of metal surface with more protective films [12].

Table 6 below represents the surface coverage of the nitrite as an inhibitor and molybdate as an additive and the synergism parameter calculated from the following formula:

Synergism parameter (S_1) = $\frac{1 - \theta 1{+}2}{1 - \theta' 1{+}2}$

Table 6 surface coverage of the inhibitor, additive, the blend and the synergism parameter

Conc. of the blend (g/L)	θ of inhibitor	θ of additive	θ_{1+2}	θ'_{1+2}	S1
0	0	0	0	0	0
2+2	0.65	0.53	0.41	0.93	8.48
2+4	0.78	0.56	0.59	0.96	10.37
2+6	0.90	0.57	0.75	0.97	8.19
2+8	0.89	0.70	0.99	0.96	0.24
2+10	0.93	0.69	1.04	0.91	-0.44

It is clear from table 6 above that the S1 was greater than one, which indicates the effect of synergism, except at concentration ratios of 1:4 and 1:5 respectively. At concentration ratio of 1:1

the S1 was 8.48 at concentration ratio of 1:2 the S1 was 10.37. However, a further increase of molybdate concentrations to 6, 8 and 10 g/L results in a decrease in S1. This shows that the optimum ratio of the blend was considered to be 1:1.

Figure 10 illustrates the comparison of the resulted efficiencies of nitrite, molybdate and the blend of the two inhibitors.

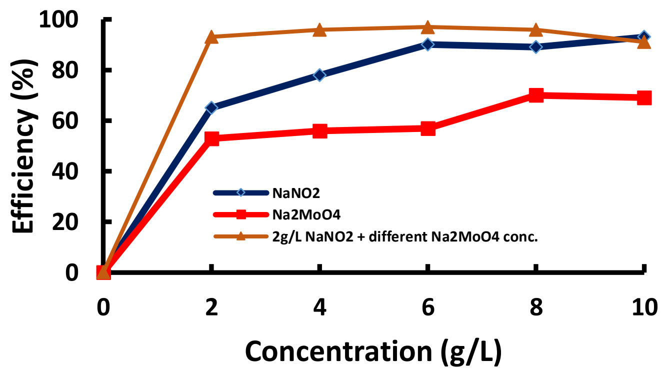

Figure 10 Efficiencies vs. concentrations

Figure 10 represents the efficiencies of the inhibitor ($NaNO_2$), the additive (Na_2MoO_4) and the blend of different concentrations. At the first step of concentration (2 g/L) the difference in efficiencies is noticeable and clear.

3.5 Scanning Electron Microscopy (SEM) Analysis

Figure 11 below shows the typical SEM images obtained for the carbon steel samples tested in blank and in nitrite solutions. The morphological examination results in Figure 11 confirm the significant effect of $NaNO_2$ inhibitor in corrosion rate reduction.

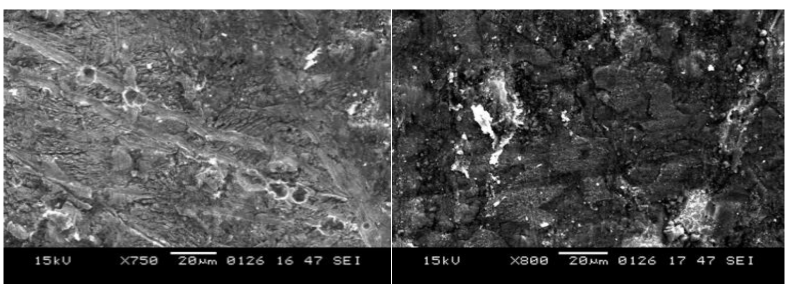

Figure 11 SEM images (**A**) and (**B**) of samples in blank and in 8 g/L $NaNO_2$

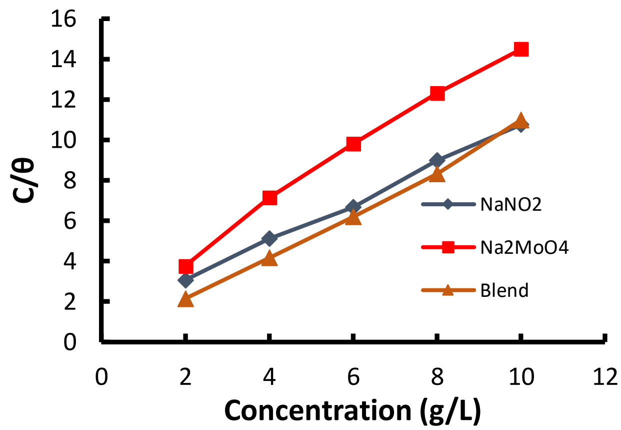

Figure 12 Langmuir adsorption isotherm of $NaNO_2$, Na_2MoO_4 and the blend

The surface coverage of the metal surface by the adsorbed inhibitor is expressed by the term θ. Plot 12 denotes different concentrations of the inhibitor, additive and the blend versus C/θ was constructed and that represents the Langmuir adsorption isotherm. It can be noticed from Figure 12 that the blend adsorption isotherm follows the Langmuir isotherm and that could be attributed to interactions between the blend adsorbed species on the metal surface [12].

4. Conclusions

The results from this work leads to the following conclusions:

- The corrosion rates decreased by increasing the NO_2 inhibitor concentrations.
- When used NO_2 alone as inhibitor, an optimum concentration of 6 g/L was achieved (efficiency = 90%).
- Molybdate alone did not give a very good effect especially at low concentrations.
- The formulation consisting of 2 g/L of $NaNO_2$ and Na_2MoO_4 (1:1 ratio) has 93% inhibition efficiency.
- The inhibition of carbon steel by $NaNO_2$ and the ($NaNO_2$+$NaMoO_4$) was attributed to the formation of a protective layer (film) on the surface.

- From the synergism parameter values (S1) > 1 indicates the synergistic effect of the blend and subsequently there was improvement of the inhibition efficiency.

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