



EVALUATING THE INHIBITIVE SYNERGY OF DI-ANODIC INHIBITORS IN ABATEMENT OF LOW CARBON STEEL CORROSION IN COOLING WATER SYSTEMS

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ABSTRACT

This study is an attempt to appraise the synergy in inhibitive effect of di-anodic sodium nitrite–borax mix on the abatement of low carbon (mild) steel corrosion in simulated cooling water system at various concentration of inhibitors by weight loss analysis. Inhibition of corrosion and scaling in cooling water systems is of continuing importance, particularly in view of the increasing demand for more efficient cooling and plant reliability in industrial applications. The efficiency of inhibition of nitrite-borax blend was 92% in a combined solution of 1000ppm NaNO_2 and 1000ppm $\text{Na}_2\text{B}_4\text{O}_7$ at 27°C room temperature which resulted in a corrosion rate of 0.0178mpy, whereas separately these inhibitors at the same dosage produced efficiencies of 47% and 45% respectively but with same corrosion rate of 1.8917mpy. The results obtained indicated that, adsorption of nitrite-borax blend occurs by chemisorption and thus follows the Langmuir isotherm model where the slope of the linear logarithmic plot approximates unity (0.9978).

KEYWORDS: *appraise, inhibition, chemisorption, corrosion, nitrite, borax, cooling water*

1. INTRODUCTION

Corrosion is the spontaneous destruction of metals (alloys) caused by chemical, biochemical, and electrochemical interaction between the metals and their environment [1]. This loss of metals by environmental factors is the main problem for the industrial companies. Since it is a natural phenomenon, it is often difficult to eliminate completely. Therefore, corrosion plays a significant nuisance in cooling and heating water systems as it is the major reason of failure of closed-loop systems. Corrosion in closed-loop systems is caused by the reaction between dissolved oxygen and the substrate metal, galvanic activity between two

different metals, low pH, or from the byproducts of bacterial activity. The dissolved oxygen in the water will start to react with steel bearing metals in the system as the temperature of the water increases. Corrosion, therefore, results in the formation of metal oxides, which affect the water quality by turning it to black water or brown sludge. This phenomenon has a significant economic effect. Many drinking water and process water transporting pipelines have corrosion troubles in open and closed tubes or cooling and heating processes. This is due to the fact that structural metals, such as stainless steel, carbon steel, copper and aluminium are liable to corrosion as a result of poorly

conditioned water. Carbon (mild) steel as construction material is widely used due to its economic viability and fair quality. However, the major drawback of using mild steel is its low resistance to corrosion in these environments [2].

A corrosion inhibitor is any chemical substance which when added to a solution (usually in small amounts) increases the corrosion resistance. Corrosion inhibitors modify electrochemical reactions by their action from the solution side of the metal/solution interface, and the increase in corrosion resistance can be measured by various parameters [1].

Corrosion inhibitors often play an important role in water treatment systems, chemical manufacturing, heavy manufacturing, oil and gas exploration and production, petroleum refining, and processing industries where they have always been considered to be the first line of defence against corrosion. Corrosion inhibitors interfere with the corrosion mechanism in order to prevent or mitigate it. Determining the most effective corrosion inhibitor for a given environment is essential, therefore, inhibitors' cost, toxicity, availability and their friendliness to the environment should be taken into account.

A variety of inorganic inhibitors have been used to reduce the corrosion rate of metallic materials in halide media [3], acidic solutions [4], neutral media [5] and in industrial waters [6]. Nitrite as an inorganic inhibitor has attracted a great deal of attention in the literature due to its low cost and relatively good inhibition performance. The anodic inhibitors such as nitrites, chromates, phosphates, borates etc., retard the anode reaction by means of oxidation on the steel surface with adsorption and reacting with the oxidizing ions or dissolved oxygen. Toxicity of chromates has restricted its use in recent years therefore prompting the search for new anodic inhibitors [7]. Adsorption and passivation results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution, thus diminishing the corrosion rate.

Although many methods have been employed to prevent the corrosion of steel, but the use of inhibitor is the most convenient and economic method in liquid-containing system such as in boiler, condenser, heat exchanger, pipelines, petroleum industries and other chemical processing industries. Cooling and heating water systems as opined by [3] are used in many public industries to heat up or cool down the equipment and unit operations. Kim, et al [8] in [9] reported that the corrosion resistance of a carbon steel pipeline was improved by adding nitrite ions, which increased the corrosion potential and decreased the current density by forming a passive film. The carbon steel pipeline

immersed in synthetic tap water containing 100 ppm nitrite ions was more susceptible to pitting corrosion than that immersed in synthetic tap water containing 50 ppm of the ions due to the effect of the small anode and large cathode area. In the work of Garces [10], the influence of pH on the nitrite corrosion inhibition of reinforcing steel bars in simulated concrete pore solution was studied and it was reported that the addition of nitrite ions inhibited the corrosion of steels in alkaline to neutral solutions although the effect depended on the nitrite concentration. However, the efficiency of inhibition was reportedly very good when the quantity of nitrite was small, but that no significant improvement resulted from further increase of the nitrite concentration from 0.1 M. Therefore attempt at surpassing the critical concentration produced contrary effect of increasing the corrosion rate. This is in agreement with [11] that nitrite concentration strongly depends on the pH range and the chloride contamination of the solution that was utilized in the operational conditions. Negative effect may be attained by addition of excessive amounts of nitrite at low pH values because of the great influence of hydroxyl groups in the inhibition mechanism of nitrite.

In the present study, separate concentrations (0.1%, 0.2%) of borax and sodium nitrite and a 0.1% blend of both were investigated in tap water in an attempt to simulate industrial cooling systems. The adsorption thermodynamic parameters and isotherm behaviour have been obtained based only on the concentration of sodium nitrite.

2. EXPERIMENTAL

Commercial ribbed mild steel rod of chemical composition (wt. %: 0.14C, 0.35Mn, 0.27Si, 0.03P, 0.025 S, and the rest Fe) used in this investigation was procured from Universal Steels, Ogba in Lagos, from where the chemical analysis was also done.

The rod was uniformly lathe-turned to about 8.80 mm diameter and thereafter 42 cylindrical test specimens of average height of about 11.00 mm cut out. The tap water used was obtained from the normal distributed supply water from water treatment department of Obafemi Awolowo University Ile-Ife and its chemical analysis is presented in table 1.

About 25g of sodium nitrite (NaNO_2) and 30g sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) analytical grade reagent obtained from Chemistry Laboratory were used as inhibitors. The 0.1wt% and 0.2wt % solutions were separately prepared by dissolving weighed 1.0g and 2.0g respectively of the anhydrous salts in 1000mls (1 litre) of tap water.

Table 1: Tap water analysis.

Component	Concentration/Value
Total Dissolved Solids (TDS)	570 ppm
Chloride Cl ⁻	5 ppm
Sulphate, SO ₄ ²⁻	25 ppm
Total alkalinity (expressed as CaCO ₃) hardness	60 ppm
Dissolved oxygen	7.2 ppm
Methyl orange alkalinity	230 ppm
pH	6.83
Temperature	25°C

The resulting solutions had concentrations of 1.45x10⁻² M and 2.90x10⁻² M for the nitrite and 2.62x10⁻² M and 5.24x10⁻² M for borax respectively.

The surface of each specimen was filed, ground and then polished under running tap water using emery paper of grade numbers, 220, 320, 450, and 600. The resulting cleaned-surface specimens were thoroughly swabbed with cotton wool soaked in phenol free acetone for degreasing and then dried with tissue paper. Finally they were labelled and kept in a desiccator over silica gel until use. Before immersion each sample was weighed accurately to the fourth decimal using Mettler weighing balances and the weight recorded.

Each of the 42 cylindrical coupons in groups of seven was completely immersed by nylon thread into test media for a duration of 14 days (336 hours). A test specimen was extracted from each of the six test media at the expiration of 48 hours interval until the 14 days elapsed. After each test, the specimens were washed under running tap water, scrubbed with a brush to remove adherent corrosion products, dried and reweighed. For the cylindrical coupons an average total surface area of about 425.8038 mm² was exposed to corrosion attack.

3. RESULTS AND DISCUSSION

3.1 Results

Table 2: Corrosion rate parameters of samples.

Sample No.	Weight loss (mg)	Time (hr.)	Corrosion rate (mpy)	Group mean corrosion rate (mpy)/ Medium	% IE	pH	Conc. (C) (mol/Litre)
1	10	48	3.462	3.4729 Uninhibited tap water (Control)	36	6.83	1.4791x10⁻⁷
2	25	96	3.383				
3	40	144	3.501				
4	57	192	3.628				
5	70	240	3.574				
6	68	288	3.43				
7	65	336	3.332				
8	8	48	2.615	1.8917 (0.1 wt.% Nitrite solution)	47	7.05	8.9125x10⁻⁸
9	18	96	2.423				
10	24	144	2.104				
11	43	192	1.86				
12	50	240	1.532				
13	54	288	1.474				
14	55	336	1.234				
15	3	48	0.724	0.4941 (0.2 wt.% Nitrite solution)	72	7.65	2.2387x10⁻⁸
16	9	96	0.664				
17	10	144	0.537				
18	12	192	0.525				
19	14	240	0.52				
20	114	288	0.512				
21	15	336	0.497				
22	9	48	2.658	1.8917 (0.1 wt.% Borax solution)	45	6.74	1.8197x10⁻⁷
23	20	96	2.412				
24	25	144	2.122				
25	44	192	1.708				
26	50	240	1.521				
27	51	288	1.415				
28	50	336	1.406				
29	4	48	1.005	0.5889			
30	10	96	0.771				
31	15	144	0.715				

32	16	192	0.584	(0.2 wt.% Borax solution)	68	7.13	7.4131x10⁻⁸
33	16	240	0.56				
34	17	288	0.487				
35	17	336	0.406				
36	2	48	0.143	0.0178 (0.1 wt.% Nitrite+0.1 wt.% Borax solution)	92	8.93	1.1749x10⁻⁹
37	2	96	0.132				
38	2	144	0.127				
39	2	192	0.122				
40	3	240	0.119				
41	3	288	0.101				
42	3	336	0.097				

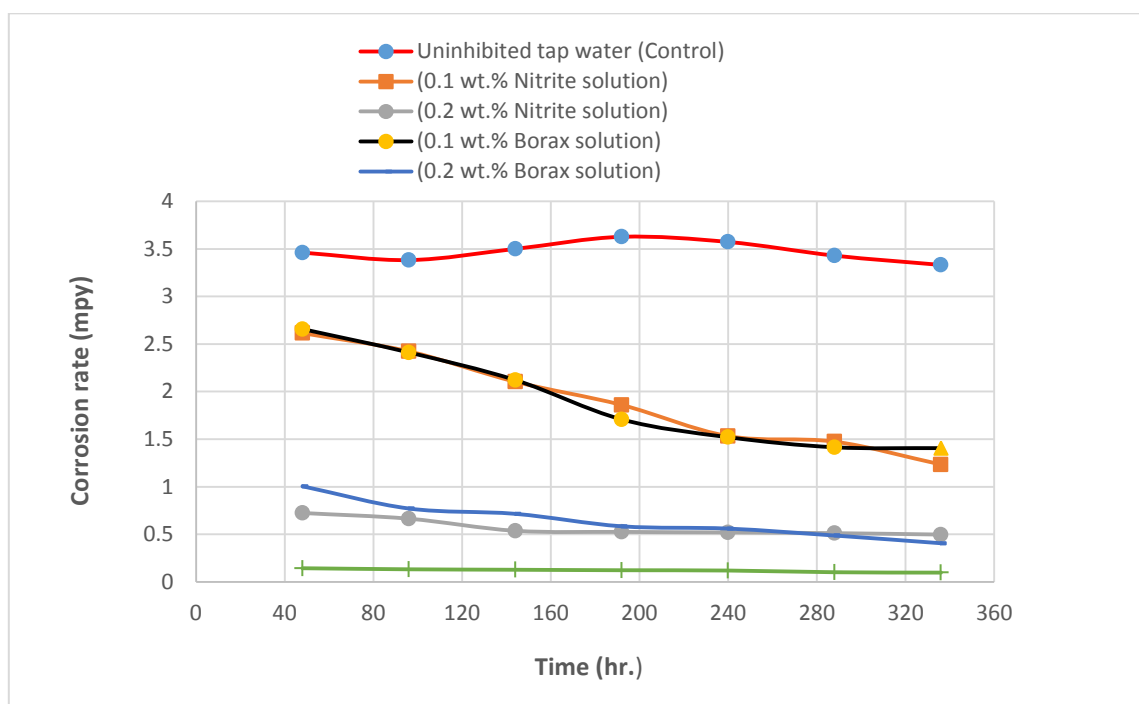


Figure 1: Corrosion behaviour of mild steel in different test media at various exposure time

Table 3: Adsorption isotherm parameters

θ	$\frac{\theta}{1-\theta}$	C (x 10 ⁻⁷) mol/L	$\text{Log} \frac{\theta}{1-\theta}$	Log C
0.36	0.5625	1.47910	-0.2499	-6.83
0.47	0.8868	0.89125	-0.0522	-7.05
0.72	2.5714	0.22387	0.4101	-7.65
0.45	0.8333	1.81970	-0.0792	-6.74
0.68	2.1250	0.74131	0.3274	-7.13
0.92	11.500	0.11749	1.0607	-8.93

3.2 Discussion of Results

3.2.1 Effect of inhibitors concentration

As can be seen from the resulting plots, the corrosion rate of the uninhibited medium (water) naturally was more (3.4729 mpy) than the other media for the following reasons. The presence of dissolved ions as contained in the water analysis (table 1) especially chlorides coupled with increased dissolution of oxygen, which is a strong oxidizer, were the direct cause of the corrosive attack of the uninhibited tap water. As observed during the experiment, progressive colour change from clear solution to brown relative to the inhibited media exposure time increased. This was

due to progressive release of various states of iron ions in (FeO, Fe (OH)₃ and Fe₃O₄ from +2 to +4 respectively. Although in soft water (as in this case) the corrosion rate usually increases at higher temperature but in moderate calcium hardness the rate of uniform attack in cooling water systems is generally reduced by scaling. Also corrosion decreases with increasing alkalinity or pH. At 0.1 wt.% concentration of inhibition both nitrite and borax separately were insufficient to effectively cover the metal surface and minimize corrosion hence they both have higher rates of 1.8917mpy each as observed in fig.1. At higher separate dosage of 2000ppm (0.2 wt.%) the rate of corrosion drastically decreased to

0.4941mpy and 0.5889mpy though patterned in similar trend as in the lower dosage.

The effectiveness of the di-anodic inhibitor blend is reflected in the plot where a synergistic effect of this mixture containing 1000ppm (0.1%) each of both inhibitors suppressed the rate of attack of the medium to 92% efficiency with the lowest corrosion rate of 0.0178 mils per year. Figure 2 shows a comparative plot depicting the relative corrosion rates and inhibition performances of the various media. Nitrites and borax generally compete neck to neck in performance at the same concentration. The inhibition efficiency increases with increase in inhibitor’s dosage. This is expected in view of the fact that the addition of inhibitor molecules to the corrosive medium lead to the replacement of the corrosive ions by the inhibitor molecules which in turn increased their protection efficiency. The effectiveness of compounds as inhibitors has been shown by [12] to be due to the ability of their oxides to be preferentially adsorbed at the metal surface in a number of oxidation and adsorption mechanism. Corrosion inhibition properties are directly related to the adsorption layer and tenacity of the oxide film. The adsorption efficiency of nitrite as an oxidizer as well as borate depends on their abilities to oxidize the mild steel surface thereby rendering it passive. It was reported by [13] that nitrite maintains a protective layer even in the absence of oxygen.

3.2.2. Adsorption Isotherm

Adsorption isotherm relates the concentration of the inhibitor in solution to the amount taken up by the

surface. To obtain the isotherm, the fractional surface coverage value, θ as a function of inhibitor concentration must be obtained. The values of θ was calculated from the following equation:

$$\theta = \frac{\%IE}{100} \tag{1}$$

Attempts were made to obtain an appropriate adsorption isotherm by fitting these θ values to various isotherm including Frumkin, Langmuir, Temkin, and Freundlich. The Langmuir isotherm was found to be the best description of the adsorption behaviour of the studied inhibitors. Using Langmuir isotherm, θ is related to the equilibrium adsorption constant (K_{ad}) and concentration of inhibitors (C), by the following equation:

$$K_{ad}C = \frac{\theta}{1-\theta} \tag{2}$$

Using Eqn. (2), the adsorption parameters were evaluated for the plot of $\log C$ against $\log (\frac{\theta}{1-\theta})$ in fig.2 to give a gradient of 0.9978, which approximates unity and therefore confirms the Langmuir isotherm model.

3.2.3. Passivation-adsorption mechanism

All metals develop a diffusion barrier layer of reaction products on the surface, which is referred to as a passive film. These reaction products are mainly metal oxides. The resistance of these films to dissolution is related to their physical and chemical nature, which determines the corrosion resistance of the metal. Furthermore, the formation of metal oxides films were explained by two theories [12].

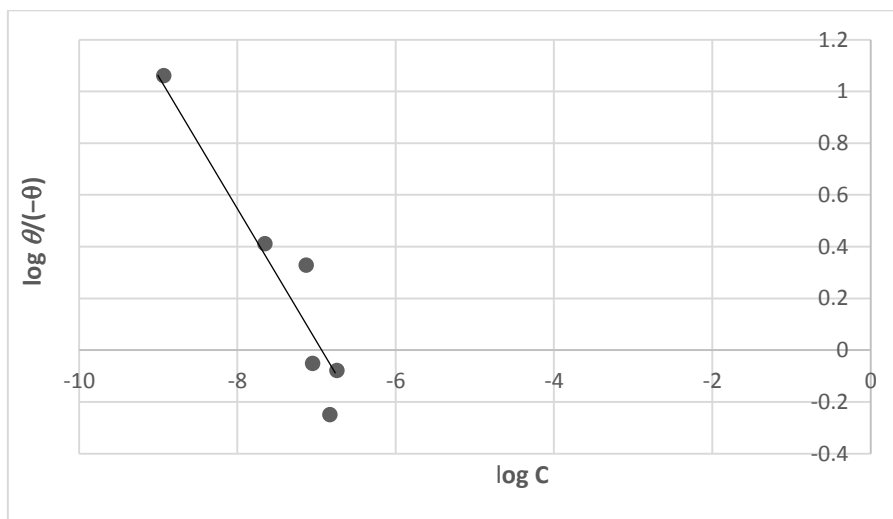


Figure 2: Graph of log C versus $\log (\frac{\theta}{1-\theta})$

Adsorption is a surface phenomenon exhibited by solids which consists of the adhesion in an extremely thin layer of the molecules of gases, of liquids, or of dissolved substances with which they are in contact. In chemisorption, a single layer of molecules, atoms, or ions is attached to the surface by chemical bonds and is essentially irreversible. In physical adsorption, attachment is due to weaker van der Waal’s forces,

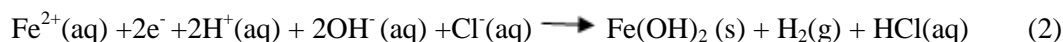
whose energy levels approximate those of condensation [12].

First passivation occurs then followed by adsorption on the metal surface using the anodic inhibitors, such as borates, nitrites and chromates, [13].

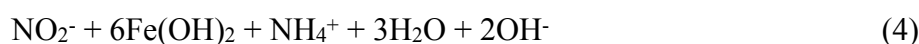
Anodic inhibitors are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with the metal ion. They are

adsorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate. Igual et al, [7] reported that, the halogen ions facilitate inhibitor adsorption and the addition of halides strongly increases the inhibition efficiency of chromates.

In this investigation, inhibition mechanism occurred first by the process of passivation and then $Fe \longrightarrow Fe^{2+} + 2e^{-}$;



The acid is concentrated with pH lowering to near 3 or 4 by gravity in puddle or pits, which further accelerates the corrosion at the site. Hence, the effect of borax addition shifted the pH to 8.93 or 9, since sodium nitrite is relatively ineffective at pH below 6. Also, the presence of $B_4O_7^{2-}$ makes Fe-O and NO_2 - Fe_2O_3 bonds



4. CONCLUSION

The inhibition efficiency of sodium nitrite-borax blend was found to be more than that of individual sodium nitrite or borax on mild steel in the simulated experiment. This study is an attempt to appraise the synergy in inhibitive effect of di-anodic sodium nitrite-borax mix on the abatement of low carbon (mild) steel corrosion in simulated cooling water system at various concentration of inhibitors by weight loss analysis. Inhibition of corrosion and scaling in cooling water systems is of continuing importance, particularly in view of the increasing demand for more efficient cooling and plant reliability in industrial applications. The efficiency of inhibition of nitrite-borax blend was 92% in a combined solution of 1000ppm $NaNO_2$ and 1000ppm $Na_2B_4O_7$ at 27°C room temperature which resulted in a corrosion rate of 0.0178mpy, whereas separately these inhibitors at the same dosage produced efficiencies of 47% and 45% respectively but with same corrosion rate of 1.8917mpy. The results obtained indicated that, adsorption of nitrite-borax blend occurs by chemisorption and thus follows the Langmuir isotherm model where the adsorbents being energetically homogeneous (all adsorption sites are equivalent) causes the heat of adsorption of the inhibitors to be independent of the surface coverage. Consequently a linear log-log plot was obtained in Figure 2, whose slope approximates unity (0.9978).

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adsorption of nitrite (NO_2^{-}) in the metal oxide layer which is facilitated by borate ($B_4O_7^{2-}$). As the corrosion starts at the tiny active sites, hydrolysis and precipitation of the less soluble Fe^{2+} hydroxides produce increase in the concentration of hydrochloric acid by the following reaction:

strong. The mechanism of passivation-adsorption due to oxidation of ferrous hydroxides to ferric oxides by nitrite ions and its deposition on the mild steel surface, as well as the adsorption of NO_2^{-} in the oxide layer proceeded according to the following reaction:

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