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1.1Aqueous Corrosion Inhibition Studies Of Mild Steel Alloy By Oxyanion Esters Of A-Hydroxy Acids And Their Salts

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Abstract

In this investigation, corrosion inhibition of mild steel in aqueous solutions has been tested primarily via weight-loss tests for their direct corrosion inhibition efficiencies and also for their conversion coating formation abilities. Effects of variables such as inhibitor concentrations, immersion periods, and cationic constituents on the individual and synergistic inhibition efficiencies as well as on their conversion coating formation capacities have been studied. Inhibition efficiency data were recorded using statistics. Some of the studied inhibitors were noted for their very high inhibition efficiencies and a few for their unusual conversion coating formation capabilities. Using the data available in literature and the experimental data obtained in this study, aqueous corrosion inhibition mechanisms of mild steel by oxyanion esters of α-hydroxy acids and their salts are suggested.

Key words: conversion coating, inhibition efficiency, weight-loss, immersion

1.1 Introduction

Corrosion inhibitors that were tested in this investigation were synthesized via a single precursor method that are described in detail along with characterization studies in author's previous studies that are available in the literature. Common characteristics of these inhibitors are that they are environmentally friendly metallo-organic corrosion inhibitors for protection of mild steel and certain aluminum alloys aimed to replace hexavalent chromium based corrosion inhibitors. For this reason, several corrosion inhibiting species such as hydroxyacids and metal oxyanions were combined in a single compound with the general formula, (M)x(hydroxyacid)y(M‘aOb)z. These were tested alongside the individual components in order to determine whether there were any synergistic interactions. It is also important to note that most of the chosen individual components are corrosion inhibitors that were previously commercialized. Some of these species such as gluconates were commercially available resulting in their direct use with no synthesis required. The common commercial use for these readily available gluconates is in the field of medicinal health as nutritional supplements. Such gluconates of zinc, calcium, magnesium and sodium were used and tested throughout this study as corrosion inhibitors, precursors, or constituents of synergistic corrosion inhibitor formulations. Readily available compounds could be further categorized based on their use as corrosion inhibitors, precursor, or both.

1.2 Weight-loss Test Method

The weight-loss method was used extensively throughout this study to assess inhibition efficiencies of corrosion inhibitors. Using metal coupons to assess inhibition efficiencies is the oldest and simplest method in monitoring of corrosion.[1] Coupons are described as small pieces of metal, usually of rectangular shape, which are inserted in the process stream and removed after a period of time that is greater than 24 hours.[2,3] The most common and basic use of coupons is to determine average corrosion rate over the period of exposure.[4] This is accomplished by weighing the degreased coupon before and after immersions followed by its exposure to various acidic solutions to remove corrosion deposits on the substrate surface. The difference between the initial and final weights of the coupon, that is the weight loss, is compared to the control. The control coupon is the substrate of the same metal alloy exposed to the same environment with no inhibitor present. At least two, and preferably more specimens should be exposed for each condition.[5] The reasons why the weight-loss method has been chosen to assess inhibition efficiencies were first, tested inhibitors are all water soluble and second it is easy to obtain accelerated corrosion conditions, and third small amounts of inhibitors are sufficient for testing.

1.2.1 Preparation of Coupons/Weight-loss Apparatus

For the preparation of coupons, mild steel and aluminum alloy metal sheets were cut in dimensions of 1x1 inch. A hole is drilled at the corner of the coupon so that the coupon could be hanged in solution via a durable polymeric material such as a fishing-line that does not corrode.

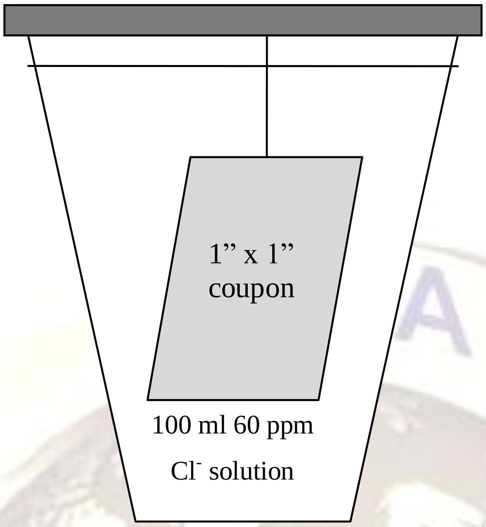

Figure Error! No text of specified style in document.**-1** Weight-loss Apparatus

Standards determined for Preparing Specimens for Weight-Loss Tests by ASTM (American Society for Testing and Materials)[6,7] were followed with no alteration. For both aluminum alloy and mild steel specimens, the first step is described as degreasing in an organic solvent or hot alkaline cleaner or both. Mild steel specimens used in this study were cut out of large rolls of mild steel sheets that were previously heavily greased to prevent them from corroding. This grease was removed from the mild steel coupons by dipping them in hexane and rubbing them with paper towels soaked with hexane when necessary. Secondly, coupons were placed in Oakite Products Inc. brand Oakite-164 alkaline cleaner solution at 150 °F for 10 minutes to complete degreasing of the coupons. Oakite solution was prepared by dissolving 60 g of Oakite detergent in 1000 ml of water at 180 °F. An additional step before performing immersion tests that is instructed by ASTM is pickling of specimen in an appropriate solution if oxides or tarnish are present in the case of aluminum specimens. After degreasing and cleaning, the coupons were weighed and fully immersed in 100 ml solutions of 60 ppm Cl^- and various concentrations of inhibitors for various periods of time (3 days, 7 days or for 14 days). As a controlled variable, 100 ml has been chosen as the volume of the solution due to the low amount of inhibitors that was required. Another controlled variable was the salt content of the solution, which was chosen as 60 ppm Cl^- since it is a situation commonly encountered in cooling water systems based on mild steel construction.[3]

Immersion periods of 3, 7 and 14 day periods were chosen since periods less than 24 hours are not enough for the system to come into an equilibrium[8], while a period of more than 14 days was too long to test many samples, that are needed for comparison purposes. Given the condition of accelerated corrosion, a period of 7 days has been determined to be the optimum period of immersion. After completion of immersion tests, coupons were exposed to an acidic solution described by ASTM to remove corrosion products for accurate weight-loss results. This solution has been prepared by dissolving 3.5 g hexamethylene tetramine in 500 ml of distilled water followed by adding 500 ml HCl. Specimens were exposed to this reagent for 10 min at 20°C to 25°C. It is indicated by ASTM that longer times may be required in certain instances; however such instances did not occur in this study meaning all specimens were cleaned of corrosion deposits thoroughly after 10 minutes of exposure. In case of specimens of aluminum and aluminum alloys, direct use of concentrated HNO_3 is inscribed by ASTM to remove corrosion deposits for periods of 1 to 5 min at 20°C to 25°C.

1.2.2 Inhibition Efficiency Calculations

Inhibition efficiencies were calculated based on the comparison of weight loss values of inhibitor treated coupons and those of controls with the following formula;

$$IE = 100[1-(W_2/W_1)]\% \quad \text{(Eq. 3.1)}$$

where

- W_1 = corrosion rate in the absence of inhibitor
- W_2 = corrosion rate in the presence of inhibitor
- W_1 & $W_2 = (W_{final} - W_{initial}) / W_{initial}$

The concentration of the inhibitors and the immersion periods were varied to obtain any possible trends of inhibition efficiencies, however inhibitor concentration of 200 ppm in 100 ml distilled water and a period of 7 days were chosen as the standard conditions after many trials as explained earlier.

Inhibition efficiency values calculated by means of the above formula were inserted into a t-distribution function formula to obtain statistically significant results. T-distribution is used rather than Z-distribution due to the low number of samples according to following formula;[9]

$$IE = \mu \pm t \frac{\sigma}{\sqrt{n}} \quad \text{(Eq. 3.2)}$$

where t is equal to the critical t-distribution value for 90% confidence limit with usually two degrees of freedom based on n, which is the number of samples. Often, only one sample has been put into test at the beginning to determine the presence of any kind of inhibition. When corrosion inhibition was observed, three more samples of the same inhibitor have been put into test, thus resulting in n = 3 and degrees of freedom, that is (n-1), equaling to 2. Critical t-distribution value for 90% confidence limit with two degrees of freedom is reported as 2.920[10].

Formulas for the mean (μ) value and standard deviation (σ) are as follows;

$$\mu = \frac{1}{n}\sum_{i=1}^{n} x_i = \frac{1}{n}(x_1 + \cdots . + x_n) \quad \text{(Eq. 3.2)}$$

$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad \text{(Eq. 3.3)}$$

The results found with inhibition efficiency formula were calculated to be statistically significant by hypothesis testing. For the inhibition efficiency values to be significant, the difference between the mean inhibition efficiency value and that of control must be bigger than the following;[11]

$$\mu - \mu_{standard} > t\left(\sigma/\sqrt{n}\right) \quad \text{(Eq. 3.4)}$$

Since there is no inhibition efficiency for control solutions, $\mu_{standard} = 0$, thus the equation is simplified to the following;

$$\mu > t\left(\sigma/\sqrt{n}\right) \quad \text{(Eq. 3.5)}$$

Insertion of critical value for t-distribution, standard deviation, and number of sample values into the above equation lead to the conclusion that mean inhibition efficiency values even for inhibitors with slight inhibition properties were statistically significant.

1.3 Categorization of Weight Loss Test Results

The weight-loss results were categorized based on the type of inhibitor, inhibitor amount in the immersion solution in ppm (part per million), chloride ion concentration in immersion solution in ppm, and the immersion period in number of days. Three immersion periods were shown in the inhibition efficiency graphs, 3 days, 7 days, and 14 days. 200 ppm is used as the standard concentration, with 25, 50, 100, and 500 ppm were other tested concentrations in addition to little used higher concentrations in molarity.

1.3.1 Gluconate Salts

All gluconate salts with the formula of $M^{+n}(X^{-1})_n$ yielded very high inhibition efficiencies both for 3 days and 7 days immersion periods with the exception $Cr(gluconate)_3$.

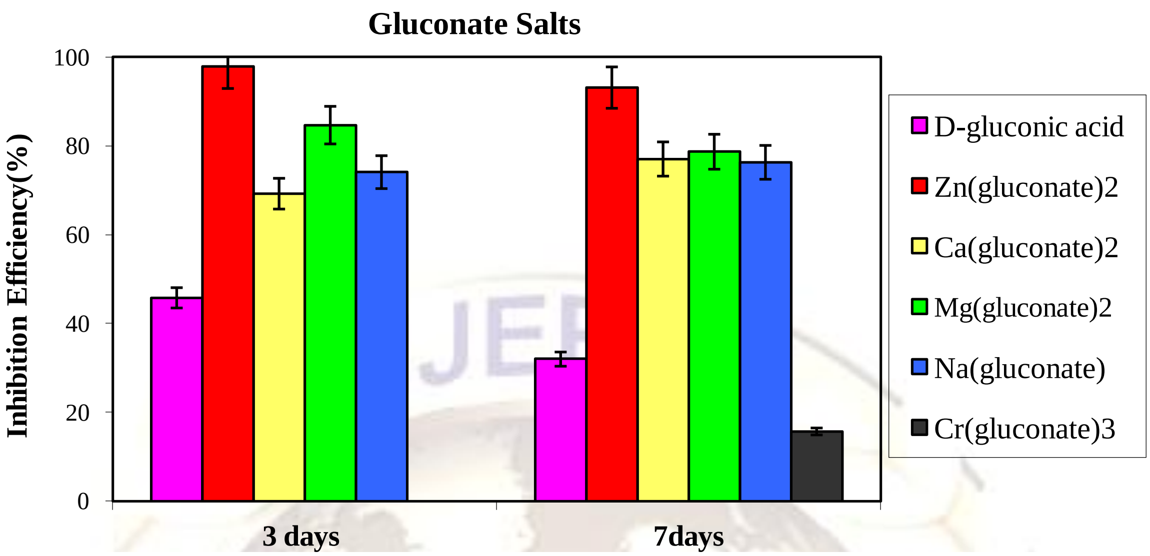

Figure Error! No text of specified style in document.**-2** Inhibition Efficiency vs. Immersion Time Graph for $M^{+n}(X^{-1})_n$ Type Gl

Zn(gluconate)$_2$ performed better than others, which was due to cathodic inhibitive activity of Zn^{+2} cations in addition to the inhibitive activity of gluconate anions. Zn^{+2} cations are known to form insoluble Zn(OH)$_2$ precipitates on cathodic sites by reacting with hydroxide ions provided by corrosion reactions of iron and thus diminish further corrosion activity. On average, only slight decreases in the corrosion inhibition efficiencies have been observed when the immersion period was increased to 3 days from 7 days in contrast to the results of a similar study indicating an inhibition efficiency of 99% for one day immersion and 65% for immersion of 5 days in 200 ppm Ca(gluconate)$_2$ solution.[3] The exception of low inhibition efficiency of chromium gluconate can be explained with strong complexation of chromium with gluconates; which as a result prevented complexation of iron cations with gluconates, thus leading to no positive effect. Notably, D-gluconic acid also inhibited corrosion with an average inhibition efficiency of 40% despite being an acid with a pKa of 3.86.[12]

1.3.2 Group III Gluconates and D-Glucose

The inhibition effciciency of Al(gluconate)$_2$OH was high comparable to the $M^{+n}(X^{-1})_n$ type gluconate salts, while B(gluconate)$_2$OH showed only slight inhibitive activity.

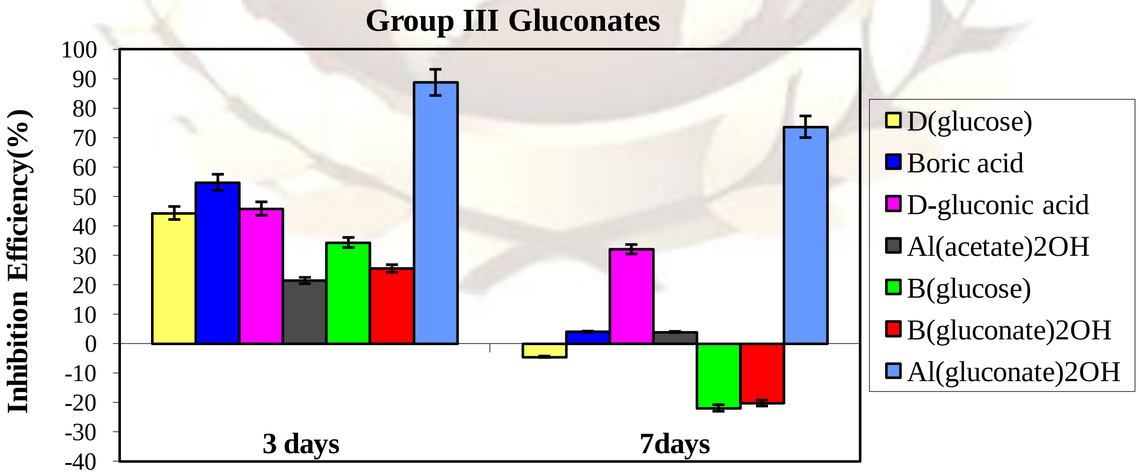

Figure Error! No text of specified style in document.**-3** Inhibition Efficiency vs. Immersion Time Graph for $M^{+n}(X^{-1})_{n-1}OH$ Type Gluconates

Gluconate's and D-glucose's corrosion inhibiting abilities were lowered by coupling with the Boron constituent. Also boric acid performed better than borogluconate and boroglucose. Thus, it was concluded that boroglucose and borogluconates were in fact not synergistic formulations. Similarly negative results were predicted for Al(gluconate)$_2$OH, opposite to what was observed. This difference was due to the exceptionally strong bonding between gluconate and borate as opposed to aluminum or it may be due to the influence of the aluminum ions themselves[13].

1.3.3 Application of Other $M^{+n}(X^{-1})_{n-1}$OH and $M^{+n}(X^{-1})_n$ Type Compounds

Being similar in structure to gluconates, lactate and acetate salts have also been tested. All of the salts under this category were already commercially available. Among them, lactic acid or 2-hydroxypropanoic acid, also known as milk acid, is a chemical compound that plays important roles in several biochemical processes and is produced naturally, while chromium (III) acetate is used to fix certain textile dyes, to harden photographic emulsions and as a catalyst.

Among tested salts, Al(lactate) has shown good inhibitive activity with values slightly lower to that of Al(gluconate)$_2$OH. Notably the difference was the similar to the difference between the inhibition efficiencies of D-gluconic acid and lactic acid. Al(acetate)$_2$OH was the only other compound with slight inhibitive activity.

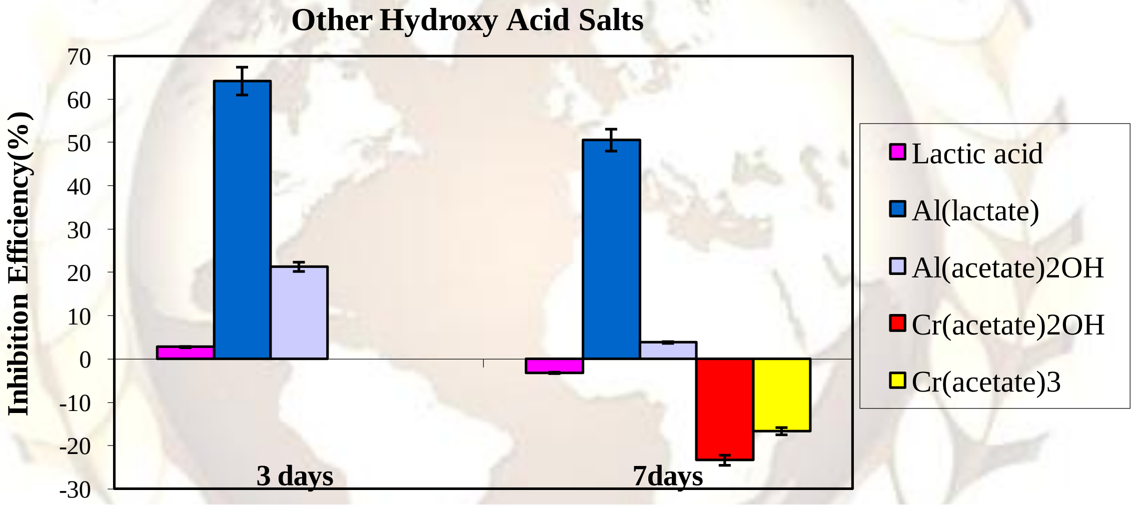

Figure Error! No text of specified style in document.**-4** Inhibition Efficiency vs. Immersion Time Graph for $M^{+n}(X^{-1})_{n-1}$OH and $M^{+n}(X^{-1})_n$ Type Hydroxy Acid Salts Other Than Gluconates

1.3.4 Molybdenum Esters of Gluconate Salts

Opposite to what had been anticipated, inhibition efficiencies of molybdenum oxyanion esters of gluconate salts were substantially lower than those of gluconate salts. Thus, metal oxyanions esters of gluconate salts were not synergistic combinations similar to borogluconates and boroglucose. Apparently, both constituents lose their inhibitive properties by forming a third product with very different chemical properties rather than a product of combined inhibitive activities of both constituents.

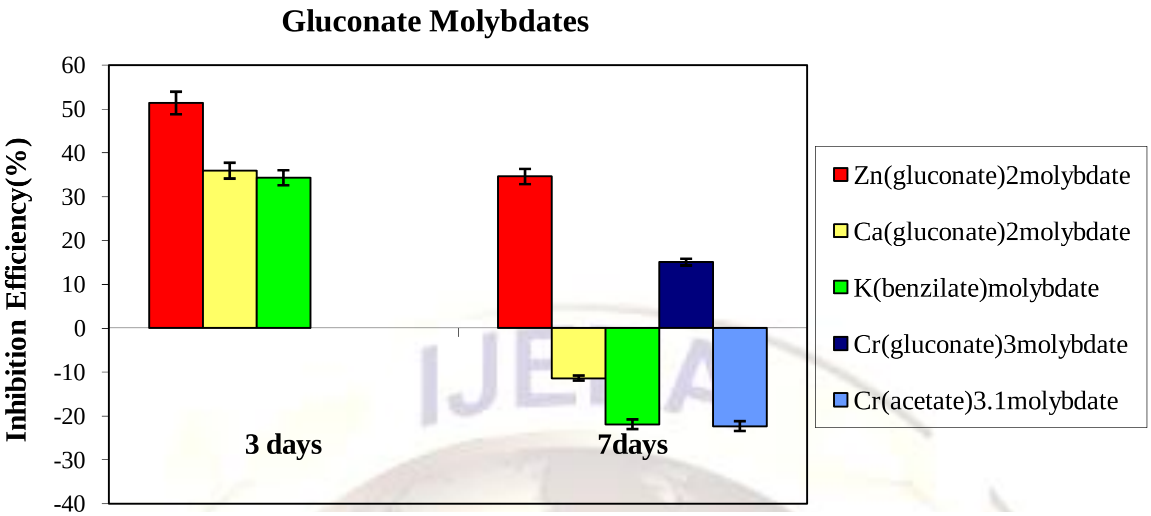

Figure Error! No text of specified style in document.**-5** Inhibition Efficiency vs. Immersion Time Graph for Molybdenum Esters of Gluconate Salts

Zinc gluconate molybdate among others has shown inhibitive activity for both immersion periods due to cathodic inhibitive activity of zinc cations included in the formulation. Both calcium gluconate molybdate and potassium benzilate molybdate have shown similar inhibitive activity during the first immersion period and none in the second, probably due to molybdate's anodic inhibitive activity which disappeared when the immersion period has been prolonged.

1.3.5 Vanadium Esters of Gluconate Salts

Inhibition efficiencies of vanadium esters of gluconate salts were also substantially lower than those of gluconate salts. Instead of being reduced to form insoluble oxides and hydroxides like chromates, vanadium constituent formed a complex compound with gluconate and benzilate which as a result diminished inhibitive properties of both constituents.

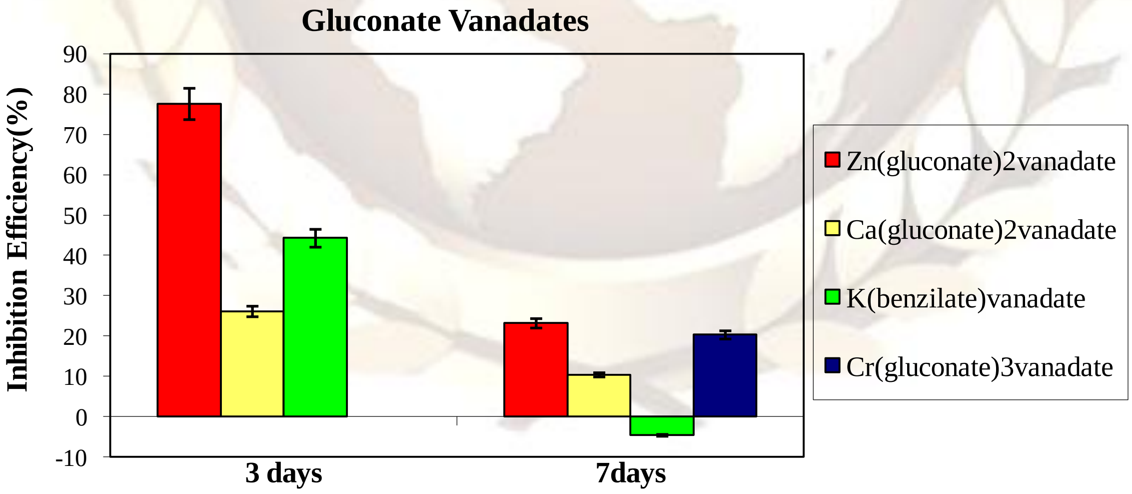

Figure Error! No text of specified style in document.**-6** Inhibition Efficiency vs. Immersion Time Graph for Vanadium Esters of Gluconate Salts

1.3.6 Boron Esters of Gluconate Salts and Derivatives

Unlike molybdenum and vanadium esters of gluconate salts, boron esters performed very well in terms of corrosion inhibition of mild steel with the exception of the borate ester of chromium gluconate.This is opposite to what had happened with the molybdenum and vanadium esters. Since the boron constituent did not diminish the inhibitive activity of the gluconate constituent. In fact, when the inhibition efficiencies for the 3 day immersion period are taken into account, the borate esters of gluconate salts performed better than gluconate salts alone indicating that combination of gluconate salts and borate constituents was a synergistic combination, where both constituents preserved their inhibitive activity.

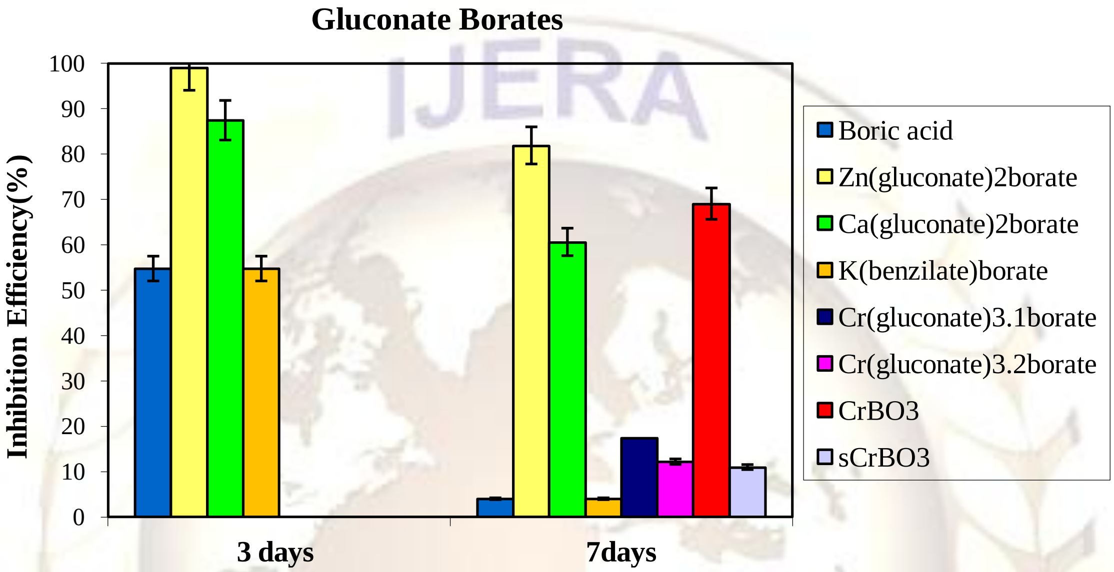

Figure Error! No text of specified style in document.**-7** Inhibition Efficiency vs. Immersion Time Graph for Boron Esters of Gluconate Salts and Their Derivatives

The facts that zinc gluconate borate had higher inhibition efficiency than calcium gluconate borate, which had higher inhibition efficiency than potassium benzilate borate implied the positive effect of the cationic constituent on the inhibition efficiency results. In fact, potassium benzilate borate had inhibition efficiencies almost same as boric acid, indicating that potassium and benzilate constituents in potassium benzilate borate were not effective on the inhibition efficiency results. These observations also revealed that cationic constituent, anionic hydroxy-acid constituent and the borate constituent synergisticly inhibited corrosion with cationic constituent having the most pronounced positive effect on the inhibition efficiency results.

1.3.7 Zinc Carboxylates

Except for Zn(tartrate) all the other compounds had negligible inhibitive activity. And that of Zn(tartrate) was likely high due to cathodic inhibitive activity of Zn cations. Surprisingly Zinc cations did not show any inhibitive activity when combined with other α-hydroxy acids. At this time, it is difficult to explain why the other α-hydroxy acids promote corrosion or are poor inhibitors.

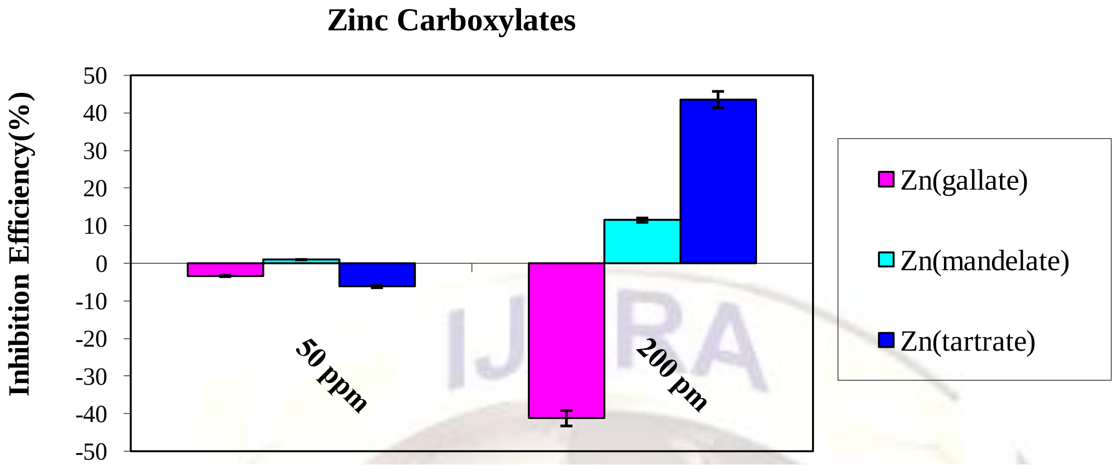

Figure Error! No text of specified style in document.**-8** Inhibition Efficiency vs. Concentration Graph for Zinc Carboxylates

1.3.8 Chromium Carboxylates

It was found that Cr(III) carboxylates do not successfully inhibit corrosion. Chromium propionate slightly inhibited mild steel corrosion, while chromium methoxy acetate inhibited more when concentrations of 25 ppm were used. However, increasing the concentration chromium methoxyacetate to 200 ppm from 25 ppm yielded negative inhibition efficiencies. The results suggest that at elevated concentrations corrosion is accelerated, possibly due to increased solution conductivity.

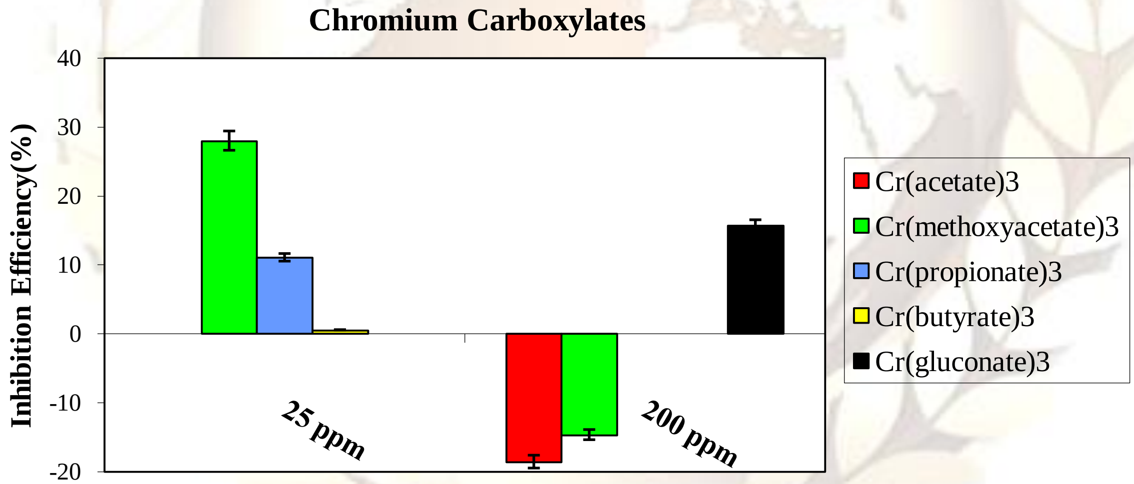

Figure Error! No text of specified style in document.**-9** Inhibition Efficiency vs. Concentration

1.3.9 Various Cr(III) compounds

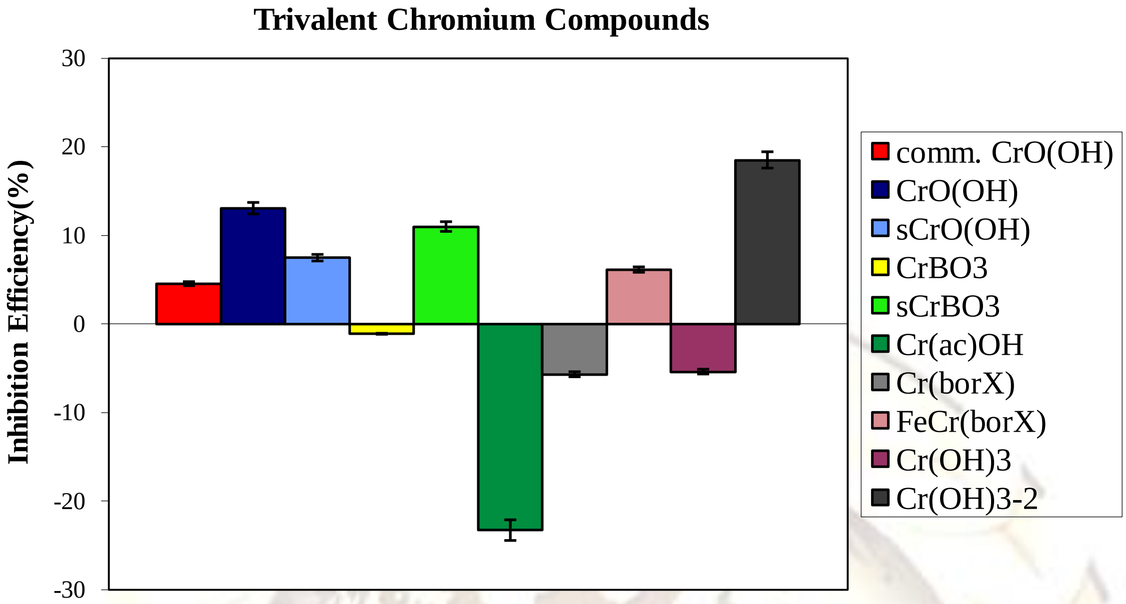

Figure Error! No text of specified style in document.**-10** Inhibition Efficiency Graph for Various

Similar to chromium carboxylates, selected trivalent chromium compounds did not inhibit corrosion of mild steel. Notably, nanoparticulate chromium hydroxide slightly inhibited corrosion while the material with larger particle size actually promoted corrosion.

1.4 Effects of Independent-Controlled Variables on Corrosion Inhibition Efficiency

The effect of independent variables that are inhibitor concentration and cationic constituents on inhibition efficiency has been examined. These variables were varied to yield higher values of dependent variables that are the final weights of the coupons (thus are the weight-losses and the inhibition efficiencies).

On the other hand, the effect of various immersion periods has also been examined. Since the controls were immersed for the same periods as the tested coupons, the immersion periods were controlled variables rather than independent variables.

1.4.1 Effect of Concentration&Immersion Periods on Inhibition Efficiency

Concentration is one of the major factors determining the inhibition efficiency. Inhibitors prevent corrosion by reacting with aggressive chemicals, preventing them to react with the metal substrates. Thus, inhibitor concentration decreases with time unless provided. Various concentrations of inhibitors were used from 25 ppm up to 500 ppm and also from 0.05 M up to 1 M for immersion tests. However, as stated earlier, among the various concentrations, the optimum concentration for an immersion test of a 1x1 mild steel coupon in a 100 ml solution of 60 ppm Cl^- was determined to be 200 ppm after many tests. Tests revealed that inhibition efficiencies generally increased with increasing concentrations up to 200 ppm and decreased thereafter. Similar observations have been reported in the literature, in which 100 ppm, 150 ppm, and 200 ppm concentrations were recorded as sufficient concentrations for corrosion inhibition in similar systems.[3]

200 ppm corresponds to a weight percentage of about 0.2%, which is in between literature values of 1%, that is claimed to be the optimum concentration of calcium gluconate tested in seawater,[14] and 0.1%, that is claimed to be the optimum concentration since higher concentrations could produce a soluble iron-gluconate complex resulting in pronounced corrosion.[15]

It has been pointed out in a previous study that zinc gluconate's inhibition efficiency decreases with increasing concentration from 200 ppm to 500 ppm due to the competition between Zn^{+2} and Fe^{+2} cations for the counter ions.[3]

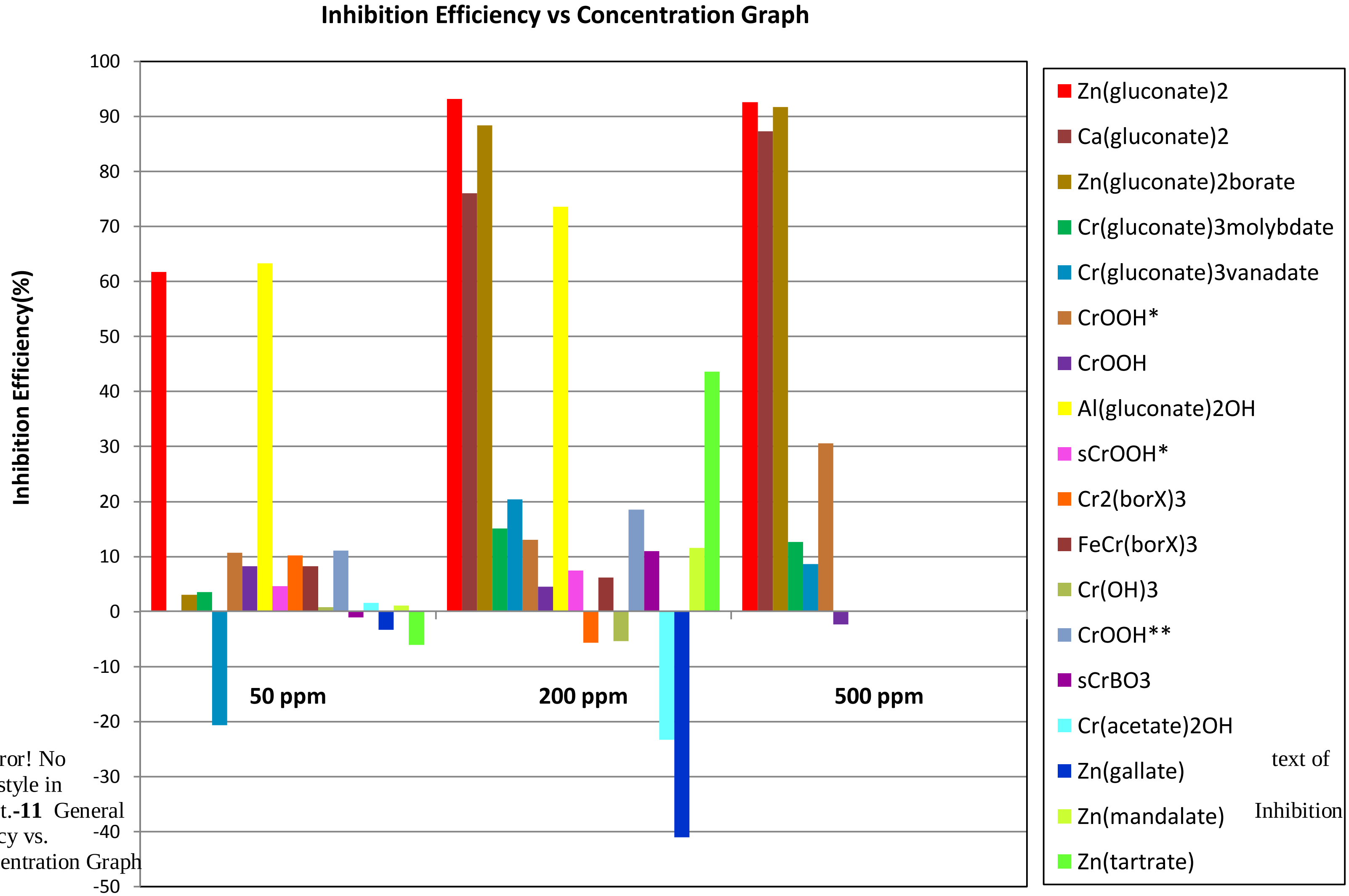

Figure Error! No specified style in document.**-11** General text of Inhibition Efficiency vs. Concentration Graph

1.4.2 Effect of Cationic Constituent on Inhibition Efficiency

Cationic constituents had considerable influence when compounds with similar anionic constituents were compared in terms of inhibition efficiencies. Zinc cations are known for their cathodic inhibitive activity in the literature. Zn^{+2} cations form insoluble $Zn(OH)_2$ precipitates on cathodic sites at high pH values due to the production of OH^{-1} by corrosion of iron substrate with dissolved oxygen. Zinc hydroxide gradually changes to zinc oxide resulting in a passive film of zinc oxides and hydroxides.[16]

$$Zn(OH)_2 \longrightarrow ZnO + H_2O \qquad \text{(Eq. 3.6)}$$

However, when chloride anions are present in the media, they react with zinc hydroxide to form soluble Zn^{2+}-Cl^--OH^- complexes[17], thus leading to breakdown of the localized passive film resulting in pitting corrosion.

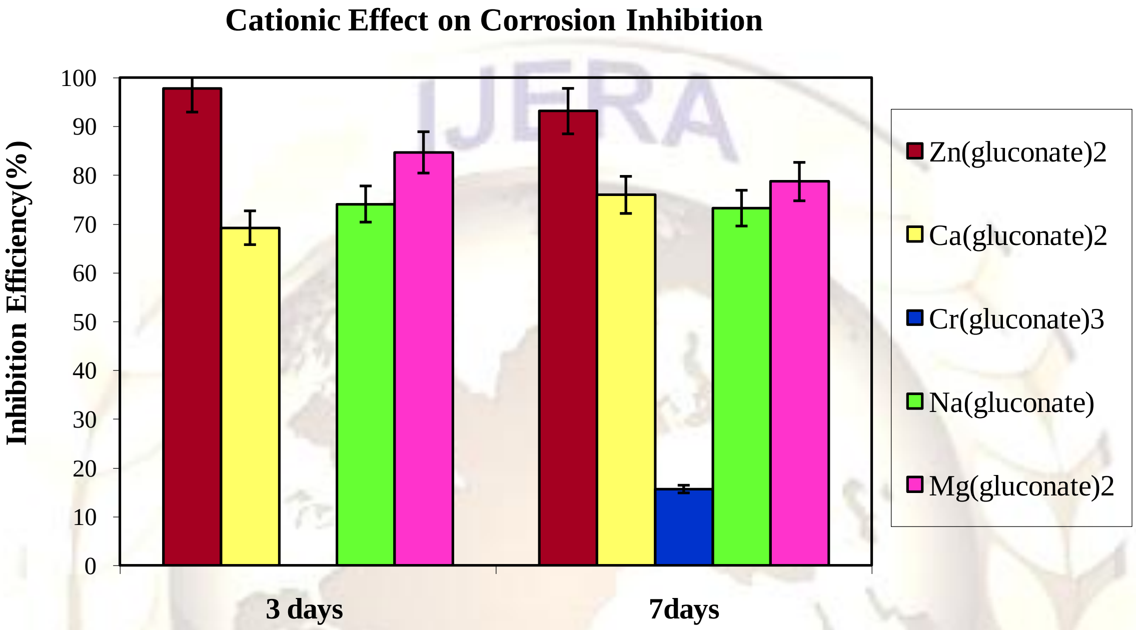

Figure Error! No text of specified style in document.**-12** Inhibition Efficiency vs. Immersion Time Graph for Formulations with Different Cationic Constituents

Figure Error! No text of specified style in document.**-13** Inhibition Efficiency vs. Immersion Time Graph for Testing Conversion Coating Formations

Other than zinc cations, calcium and magnesium ions, which constitute the hardness of water, are also known to have slight cathodic inhibitive activity due to their little soluble hydroxides especially in near neutral-basic conditions such as seawater. However, no major differences were observed in terms of inhibition efficiencies between sodium, magnesium, and calcium gluconates. The sodium cation, all of its salts being soluble, and also inert towards redox reactions is primarily considered ineffective for corrosion inhibition of any metal. It is only effective in determination of secondary solution properties such as solubility and conductivity. Therefore, this indifference between sodium, magnesium, and calcium gluconates indicate that the inhibition by gluconate was the primary mechanism of corrosion inhibition. Trivalent chromium did not seem to inhibit mild steel corrosion even when combined with metal oxyanions. If anything, Cr^{3+} either prevented the gluconate's inhibition mechanism or promoted corrosion.

1.5 Conversion Coating Formation Studies

Corrosion inhibitors prevent corrosion either by continuously reacting with the aggressive chemicals, which requires a continuous supply of the corrosion inhibitor or by forming conversion coatings on the metal surface, which protects the metal substrate for longer periods of times. Thus, in addition to direct inhibition of corrosion, the inhibitors were tested for conversion coating formations and if present, the nature of this film was studied and characterized. Notably, chromates prevent corrosion both directly and indirectly leading to the formation of conversion coatings that have self-healing abilities.

1.5.1 Using the Weight-Loss Method

To examine the coupons for conversion coating formation, coupons that previously immersed in the solutions of inhibitors were immersed in salt water with no inhibitor present for a second period of time. The presence of corrosion inhibition during this second immersion period would imply the presence of a protective conversion coating on the substrate surface.

The results revealed that for all of the gluconate-containing inhibitors there was corrosion protection present during the first 3 days of the second immersion period but the inhibition efficiency was significantly less than that found when the corrosion inhibitor was present in the solution. This suggests that the inhibition was due to inhibitors leached from deposits of corrosion products on the substrate surfaces. This was confirmed by further substantial decreases in inhibition efficiencies during the next 4 days of the second immersion periods. Upon completion of second immersion periods of 7 days, only a few inhibitors yielded positive inhibition efficiencies; among them were zinc and calcium gluconate, and aluminum gluconate hydroxide.

The weight changes of mild steel coupons after immersions into solution of $Al(gluconate)_2OH$ with or without 60 ppm Cl^- has also been measured. Less weight-loss was recorded for the coupon immersed in solution of $Al(gluconate)_2OH$ without Cl^- compared to the control coupon under the same conditions indicating that conditions with no Cl^- were favored for the formation of aluminum gluconate conversion coatings.

The slight inhibition by calcium and zinc gluconates during second immersion periods could be attributed to the same reasons explained for their inhibition efficiencies during first immersion periods. However, this reasoning cannot explain the high inhibition efficiency of $Al(gluconate)_2OH$ since for one, aluminum is not known with its cathodic activity and since, unlike calcium and zinc hydroxides, at highly basic local conditions, aluminum hydroxide dissolves due to complexation. Thus, further examination was needed using other methods such as surface characterization techniques.

1.5.2 Weight Difference Measurements

Weight changes of the coupons during immersions were determined prior to cleansing of corrosion deposits, since the presence of any type of deposition on the surface would have increased the weight of the coupon. To determine whether the increase in weight was caused by corrosion deposits or a protective coating, weights prior to the removal of corrosion deposits were compared to the weights after removal of corrosion deposits. Almost no weight-loss values were recorded for $Al(gluconate)_2OH$ and $Ca(gluconate)_2$borate treated coupons prior to the removal of corrosion products. In the case of $Zn(gluconate)_2$vanadate treated coupon's weight had increased. After the application of the cleaning solution, both $Al(gluconate)_2OH$ and $Ca(gluconate)_2$borate treated coupons still had negligible weight-losses. These results correlated with the inhibition efficiency results. Also the formation of a protective coating due to $Al(gluconate)_2OH$ was visually apparent. In the case of $Ca(gluconate)_2$borate treated coupons a possibly formed protective coating was certainly not stable since a highly negative inhibition efficiency was observed during second immersion periods. On the other hand, the $Zn(gluconate)_2$vanadate treated coupon had a significant weight-loss correlating with its lower inhibition efficiency values than those of $Al(gluconate)_2OH$, and $Ca(gluconate)_2$borate.

In conclusion boron esters and $Al(gluconate)_2OH$ had the least weight-losses during first immersions followed by vanadium, and molybdenum esters; respectively. Trivalent chromium compounds had the highest weight-loss values among all. Discussion and Conclusions

1.5.3 Discussion of the Inhibition Mechanisms of Gluconate Salts in Literature

The inhibition effect of gluconates has been discussed by several authors in the literature.[18-33] Most of the authors agree that gluconates inhibit the corrosion by influencing the anodic reaction of metal dissolution, but there is no general agreement on the mechanism of that action.[22,23,30,34,35] On the other hand, there seems to be an agreement on the contribution of the cationic constituent to the corrosion inhibition. The most commonly used gluconate salts are zinc gluconate and calcium gluconate, which form zinc and calcium hydroxides at the cathodic sites inhibiting the cathodic corrosion reaction. Initially, the cathodic corrosion reaction, that is the oxygen reduction reaction, provides the OH^- leading to increases in local pH values enough to precipitate zinc and calcium hydroxides. Thus, the process is a repassivation process. Among zinc and calcium gluconates, the effect of zinc gluconate is described as more pronounced in the literature due to the higher insolubility of zinc hydroxide.[15,24,30,34,35] The following mechanisms have been proposed for corrosion inhibition action of gluconates on iron and mild steel in near neutral solutions;[24,30,34-37]

1. Repair of the oxide film by adsorbing on the weak spots of an inhomogeneous, porous oxide film,
2. Incorporation into the oxide film during its formation,

3. Reaction with iron ions forming complexes that precipitate on the metal surface,
4. Forming complexes with iron cations while they are still bound up in the metal lattice rather than forming precipitates.

The third action mechanism among others seemed to be favored in several recent studies,[3,38] while it is being questioned by some others[25,27-30] There are other studies that favor simultaneous occurrence of both the third and fourth mechanisms, in which gluconate forms insoluble complexes weith Fe(II) cations, while at the same time forming soluble complexes with the Fe(III) cations. In these studies, it is claimed that complexation of both Fe^{2+} and Fe^{3+} with oxalate or gluconate inhibits mild steel corrosion by keeping Fe^{3+} ions in solution but forming insoluble complexes with Fe^{2+}. In one of these studies, insoluble β-$Fe(C_6H_{11}O_7)_2$ precipitate was claimed to be observed through X-ray analyses of the surfaces. However, our X-ray analyses of mild steel substrate surfaces treated with gluconates revealed peaks due only to the substrate metal and corrosion products. Also a frequency shift of the C=O peak of calcium gluconate from 1606 cm^{-1} to 1622 cm^{-1} after completion of immersion was claimed to be an evidence of precipitation of iron gluconates on the surface as well.[39-41] A similar shift in the spectra of coupons immersed in calcium gluconate solutions was observed in this study.

It is well-known that gluconic acid and gluconate salts form water-soluble complexes with most metal cations. Stability constant measurements also indicate that stabilities, thus the solubilities of these complexes increase with pH.[35]

Therefore, the differences between proposed action mechanisms is reduced to a problem of determination of the micro conditions such as whether the pH is suitable for gluconate complexes to precipitate on the metal substrate. Testing of the alloy substrates treated with inhibitor solutions for conversion coating formation revealed substantially low inhibiton efficiencies with the exception of $Al(gluconate)_2OH$. This indicates that an insoluble protective iron-gluconate film does not exist on the metal surface or it is only present when gluconate ions are provided in the solution. In practical terms, a non-stable film of iron gluconates that dissolves in very short time when no gluconate is present in the solution is equal to having no film at all since, in both cases, gluconates have to be supplied steadily. In agreement with this statement, practical applications such as the use of gluconates to eliminate iron oxide corrosion deposits in cooling water equipments[42] or as sequestering agents that prevent deposition of calcium carbonate from hard waters also requires steady supply of gluconates.[30,34,35] This fact has been implied in one of the studies of the authors who favor iron-gluconate precipitation on the substrate surface. It has been stated that the decrease in inhibition efficiency with increasing period of immersion time, from 1 to 3 days to 5 days, was due to the dissolution of the Fe^{2+}-gluconate complex formed on the metal surface.[38] In another study, it has been mentioned that concentrations by weight over 0.1% would result in soluble iron gluconate complexes.[15] This concentration corresponds to the 100 ppm of inhibitor used in weight-loss experiments in this research. Considering 200 ppm was determined to be an optimal concentration in this research, it is likely that soluble iron gluconate complexes were adsorbed on the substrate surface, thus repairing the protective oxide film rather than forming a protective coating on the substrate surface. A similar behavior of gluconates has been pointed out in a study of sodium borogluconate adsorption on an iron surface that revealed it was adsorbed on the protective oxide film and not directly on the iron.[23]

1.5.4 Suggested Inhibition Mechanism of Salts of Gluconic Acid and Other Hydroxy-Acids

Prior to the discussion of the inhibition mechanism of gluconates a few points should be considered:

Gluconate is known as a complexing agent widely used as an efficient masking reagent for cations[43]. When comparing the complexing ability of the hydroxycarboxylic acids however, a larger negative charge corresponds to stronger complexing ability, which also translates to having more carboxyl groups. Another point is that gluconic acid has a pKa of 3.86[12] therefore, it is fully ionized at near neutral conditions to gluconate, thus pH does not play any role and conjugate acid-base equilibrium of gluconate does not have to be considered. When mild steel coupon is immersed in a solution containing 60 ppm Cl^- and 200 ppm gluconate salt, the gluconate salt diffuses from the bulk of the solution to the metal surface, where initially an iron(II) gluconate complex is formed on the anodic regions and the cationic constituent of the gluconate salt is released to the solution or to the cathodic sites in the case of zinc, calcium or magnesium cations. Thus, first iron(II) cations form, driven by the negative standard reduction potential of the following reaction at ambient conditions;

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad \text{(Eq. 3.8)}$$

Normally, driven by thermodynamics, iron (II) cations oxidize quickly to iron (III) cations in water[44], leading to the corrosion products as follows;

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad \text{(Eq. 3.9)}$$

$$Fe(OH)_3 \longrightarrow FeOOH + H_2O \qquad \text{(Eq. 3.10)}$$

However gluconates form complex compounds with the iron (II) cation preventing its oxidation to iron (III) cation and preventing further corrosion reactions from taking place by stopping mass transport of ions resulting in an incomplete electrochemical cell.[43] Iron(II) cations can form monodentate or bidentate complexes with gluconates.

$$Fe^{2+} + M(gluconate)_n \rightleftharpoons Fe(gluconate)^{+} + M^{n+} \qquad (Eq.\ 3.11)$$

$$Fe(gluconate)^{+} + M(gluconate)_n \rightleftharpoons Fe(gluconate)_2 + M^{n+} \qquad (Eq.\ 3.12)$$

Other studied carboxylic acid salt and its esters, that is benzilate, also form stable complexes with iron(II) and iron(III)cations[44-46], thus same arguments that is being made for gluconates herein may as well be considered for benzilate compounds to some extent.

It is also mentioned in the literature that ligands which form complex compounds with iron cations with comparable low formation constants will cause precipitation of $Fe(OH)_2$ and $Fe(OH)_3$ in highly alkaline conditions.[48]

$K_{sp}(Fe(OH)_2 = 8.0 \times 10^{-16}$, $K_{sp}(Fe(OH)_3 = 4.0 \times 10^{-38}$ [49]

Conversion of iron gluconates to more stable iron hydroxides with increasing pH may explain the presence of weak bands due to corrosion products of iron in the IR spectra of coupons immersed in gluconate salts.

Gluconates are also reducing agents, similar to ascorbic acid although less strong, preventing oxidation of iron(II) to iron(III).[50] In addition, the formation of a more stable complex when the metal has the lower oxidation number favors reduction and as a result the reduction potential becomes more positive.[51] In this case, the comparison is with the Fe(II)hexahydrate vs Fe(II)gluconate. The gluconate complex is more stable and therefore favors remaining in the reduced state. Meanwhile, the cationic constituents such as zinc and calcium cations form insoluble hydroxides at the cathodic sites, thus lead to the blocking of the galvanic corrosion cell.

$$M^{n+} + nOH^{-} \longrightarrow M(OH)_n \qquad (Eq.\ 3.13)$$

when M = Zn, Ca, or Mg

Thus, trivalent iron gluconate formation is ruled out unless breakdown of the gluconate inhibitor occurs due to extreme conditions or if it is consumed totally. However, if present, due to conditions favoring corrosion reactions, iron (III) cations can also form stable complex compounds with gluconates preventing further corrosion reactions that involve trivalent iron.

$$Fe^{3+} + M(gluconate)_m \longrightarrow Fe(gluconate)^{2+} + M^{m+} \qquad (Eq.\ 3.13)$$

$$Fe^{3+} + M(gluconate)_m \longrightarrow Fe(gluconate)_2^{+} + M^{m+} \qquad (Eq.\ 3.14)$$

$\log(\beta_1) = 22.23$, $\log(\beta_2) = 10.51$ [52]

Iron (III) gluconates can further form complex compounds with calcium cations to form very stable water soluble products.[52]

$$Fe(gluconate)^{2+} + Ca^{2+} \longrightarrow CaFe(gluconate)^{+3} \qquad (Eq.\ 3.15)$$

$$Fe(gluconate)_2^{+} + Ca^{2+} \longrightarrow CaFe(gluconate)_2^{+2} \qquad (Eq.\ 3.16)$$

In the specific case of $Al(gluconate)_2OH$, the low stability constant of aluminum gluconate may facilitate forming of iron(II)gluconates and a protective coating of aluminum oxides/hydroxides as implied by the IR results. In addition, the greenish color that was visible on substrate surface might be due to iron(II)gluconate since iron(II) products are known to be greenish in color.

1.6 Conclusions

The combined use of metal oxyanions with gluconates have been reported to result in increased inhibition effect such as, for example, the application of sodium gluconate together with tetraborate, nitrite or molybdate.[25,27-30] Other studies reporting synergistic effects of gluconate include literature cite gluconates as scaling inhibitors that improve the action of molybdate and tungstate.[42,53]

The combination of these constituents under one formulation yielded only slightly positive inhibition efficiencies in the case of molybdenum and vanadium esters but high inhibition efficiencies in the case boron esters.

Clearly, complexation of molybdenum and vanadium constituents with gluconate led to a diminished complexing ability of the gluconates with iron cations due to highly stable complexes. Gluconate and benzilate complexes of molybdenum and vanadium with various oxidation states are reported in the literature.[54-64]

The boron esters of gluconates on the other hand produced high inhibition efficiencies. As a reason, the formation constant of boron gluconate complex is very low compared to transition metal complexes of gluconates. Hence, boron ester may facilitate the formation of iron gluconate complex due to its higher solubility compared to other gluconate salts.

Developing environmentally friendly effective corrosion inhibitors to replace carcinogenic inhibitors based on chromates is a problem that needs to be addressed in the very near future. Iron and steel are the major components of artificial structures. Thus, increasing their lifetime by limiting the corrosion to lowest possible rates is of utmost importance. Structures in aqueous environments are very common, so effective and environmentally friendly inhibitors specifically designed for mild steel corrosion in aqueous environments are needed. Corrosion of steel is commonly faced in areas such as the oil/petroleum industry, cooling water systems, mine water systems, in soils of marine environments, etc. Gluconates have become well-established corrosion inhibitors of mild steel in the last decade. In addition to their high inhibition efficiencies, the fact that they are even used as medicine for various mineral deficiencies as health supplements is a characteristic that is not common among corrosion inhibitors, which are usually based on toxic materials such as hexavalent chromium, nitrites, phosphates, etc. In this investigation, weight-loss tests with various salts have been repeated and results supporting the literature have been observed. Secondly, synergistic formulations of gluconates along with benzilates and other carboxylates such as lactate, and acetate were put into test and as a result, borate esters of hydroxy-acids, namely, calcium and zinc gluconate borates were observed as very successful inhibitors of mild steel corrosion along with zinc and calcium gluconates. Additionally, evidence supporting conversion coating formation on mild steel substrate by aluminum gluconate hydroxide was realized through weight-loss tests, infrared spectra, X-ray photo electron spectroscopy and digital imaging. Aluminum gluconate hydroxide is one of the gluconate salts and like other gluconate salts had high inhibition efficiency during regular immersion periods. However, substrates that were dipped into aluminum gluconate hydroxide solutions during first immersion periods were resistant against corrosion during additional immersions of similar or longer periods even when there was no aluminum gluconate hydroxide present in the solution.

In the light of these characterizations, the proposed inhibition mechanism of the synergistic formulations of hydroxy-acids and metal oxyanions was based on the repair of the protective oxide films on the metal substrate. Successful inhibitors such as gluconates and borates repaired the protective oxide film on mild steel substrates either by adsorbing onto the substrate surface and preventing aggressive anions to be adsorbed via competitive adsorption mechanism or by forming mild strength complexes with iron cations leading to an incomplete corrosion cell thus preventing further corrosion or by incorporating into the protective oxide film and repairing defective sites.

However, a mechanism favored by several authors in the literature, that is formation of insoluble iron gluconate complexes on the metal substrate did not seem to be possible at least not for a considerable period of time given the aggressive conditions of the media. On the other hand, supportive results were obtained concerning the proposed inhibition mechanisms of zinc, calcium, and magnesium via weight-loss tests. These cations inhibit corrosion by forming insoluble hydroxides at cathodic sites. However, no evidence was obtained by X-ray powder diffraction or infrared spectroscopy for the existence of these hydroxide phases.

1.7 Future Work

Thirdly, inhibitors that can form conversion coatings, such as aluminum gluconate hydroxide in the case of mild steel and potassium benzilate vanadate in the case of aluminum alloys, could be deposited on the substrate using layer by layer method. If successful, physical properties of the coating could be measured in addition to the tests to measure the corrosion inhibitive properties.

Surface characterization techniques, X-ray fluorescence, X-ray photoelectron spectroscopy and scanning electron microscopy could be used more for characterization of the substrate surfaces after treating them with inhibitors.

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