Characterization Studies Of Aqueous Immersion Solutions Of Novel Environmentally Friendly Organometallic Corrosion Inhibitors Used To Cure Mild Steel Substrates In Corrosive Media

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ABSTRACT

In this investigation, aqueous immersion solutions of novel environmentally friendly corrosion inhibitors that are used to inhibit corrosion of mild steel substrate surfaces in corrosive media are characterized since immersion solutions are indicators of the extent of corrosion, which can even be observed visually in a qualitative manner, e.g. salt solutions of gluconate salts remained clear throughout the immersion of mild steel coupons, while the salt solution in which the control coupon was immersed, changed its color from clear to dark brown indicating the presence of corrosion products of iron. On the other hand, the color of salt solutions of molybdenum esters of gluconate salts changed from clear to yellow and the salt solution of vanadium ester of potassium benzilate changed color from clear to light yellow indicating some corrosion was taking place. In addition to visual observations revealing the extent of corrosion qualitatively, the pH, conductivity and oxidation-reduction potential of the immersion solutions were measured with respective probes prior to and after the immersions and relevant conclusion made extensively to propose the chemical mechanisms with regards to the inhibitors used for corrosion inhibition of mild steel alloy. Inhibitors used were previously synthesized by the author as replacements for carcinogenic hexavalent chromium inhibitors. Syntheses and characterization studies of the novel environmentally friendly corrosion inhibitors, the results of weight-loss tests performed to obtain the inhibition efficiencies of these inhibitors and characterization studies of the substrate surfaces immersed in aqueous inhibitor solutions by means of different surface techniques such as FT-IR, X-Ray, SEM, XPS and digital imaging were reported in author's various work elsewhere in the literature.

Key words: carcinogenic, characterization, conversion coating, immersion, substrate

1. INTRODUCTION

The mobility of aqueous Cr^{6+} within biological systems and its reactivity with biochemical oxidation mediators make it highly toxic, carcinogenic and generally regarded as a very hazardous soil and groundwater pollutant [1-6]. Dermatitis and skin cancer have been reported among workers merely handling components protected by a chromate film [7]. Many reviews in the literature point out to toxicity of chromates associating Cr^{6+} with lung cancer. Although there is no general agreement on the details for the Cr^{6+} induced damage to DNA resulting in cancers, it is clear that Cr^{6+} is highly water soluble and it passes through cell membranes, and highly reactive intermediates such as Cr^{5+} stabilized by alpha hydroxyl carboxylates and Cr^{4+} are genotoxic and react either directly or through free radical intermediates to damage DNA [8-13]. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to humans. The World Health Organization (WHO) has determined that Cr(VI) is a human carcinogen [14]. The Department of Health and Human Services (DHHS) has determined that certain Cr(VI) compounds (calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate) are known human carcinogens [15]. Finally, the EPA has classified Cr(VI) as a Group A, known human carcinogen by the inhalation route of exposure [16-21].

However, despite their negative aspects, to date, no replacements exist in the market for carcinogenic chromates with the same efficiency for a range of aluminum alloys and steel, neither as pigment nor as a metal pretreatment [22-23]. Given the toxicity and carcinogenicity of chromates, the purpose is not only to synthesize and characterize efficient corrosion inhibitors for certain alloys of certain metals to be applied in different environments, but also to find environmentally friendly corrosion inhibitors for successful chromate replacements. In this regard, the standard for an environmentally friendly inhibitor is considered as having acceptable or no toxicity compared to chromate inhibitors. Studying the reasons underlying the success of chromate inhibitors seemed to be the first reasonable approach one might take before formulating chromate replacements, e.g., synergistic combinations of oxyanion analogues of chromates with those of hydroxyacids and metal cations that are known for their corrosion inhibiting efficiencies having the general formula of $(M)_x(\text{hydroxyacid})_y(M'_aO_b)_z$, which constituted the first phase of this research by the author [24]. Syntheses and chacaterization work was followed up with the weight-loss tests to obtain the inhibition efficiencies of respective inhibitors, while in this study, aqueous immersion solutions of novel environmentally friendly corrosion inhibitors that are used to inhibit corrosion of mild steel substrate surfaces in corrosive media are characterized.

2. CHARACTERIZATION OF IMMERSION SOLUTIONS

Immersion solutions are indicators of the extent of corrosion, which can even be observed visually in a qualitative manner, e.g. salt solutions of gluconate salts remained clear throughout the immersion of mild steel coupons, while the salt solution in which the control coupon was immersed, changed its color from clear to dark brown indicating the presence of corrosion products of iron. On the other hand, the color of salt solutions of molybdenum esters of gluconate salts changed from clear to yellow and the salt solution of vanadium ester of potassium benzilate changed color from clear to light yellow indicating some corrosion was taking place. In addition to visual observations revealing the extent of corrosion qualitatively, the pH, conductivity and oxidation-reduction potential of the immersion solutions were measured with respective probes prior to and after the immersions and relevant conclusion made extensively to propose the chemical mechanisms with regards to the inhibitors used for corrosion inhibition of mild steel alloy. Inhibitors used were previously synthesized by the author as replacements for carcinogenic hexavalent chromium inhibitors. Syntheses and characterization studies of the novel environmentally friendly corrosion inhibitors, the results of weight-loss tests performed to obtain the inhibition efficiencies of these inhibitors and characterization studies of the substrate surfaces immersed in aqueous inhibitor solutions by means of different surface techniques such as FT-IR, X-Ray, SEM, XPS and digital imaging were reported in author's various work elsewhere in the literature.

Three aluminum alloys were chosen for the corrosion inhibition tests in aqueous environments that are Aluminum 2024, 6061, and 7075 alloys due to their common use in industry and, specifically, in aircrafts.

Characterization of the immersion solutions was conducted using oxidation-reduction potential, pH and conductivity probes. Two readings were taken per sample, one before immersion and another after completion of immersion.

2.1. ORP MEASUREMENTS

ORP is proportional to the concentration of oxidizers or reducers in a solution, and their activity or strength. It provides an indication of the solution's ability to oxidize or reduce another material. The addition of an oxidizer will raise the ORP value, while the addition of a reducer will lower the ORP value.

The ORP values of immersion solutions were measured to determine whether the redox capable inhibitor compounds had gone thorugh redox reactions or not. Dissolved oxygen may be reduced by the metal substrate and leading to lowering of the ORP value but comparison to the control solution should negate this effect.

Overall, the ORP values were decreased in average by half during immersions for both the control and inhibitor containing solutions. The exceptions were the gluconate salts of zinc and calcium, and their vanadate esters, where only a slight decrease in ORP occurred. As expected, inclusions of salt ions into the immersion solutions and increasing the immersion period led to further decrease in ORP.

In contrast to the molybdenum esters of gluconate salts, the ORP values for immersion solutions of vanadium esters of gluconates did not decrease. The amount of slight decrease or even increase was approximately the same for all vanadium esters regardless of whether the hydroxy-acid constituent was gluconate or benzilate with the exception of zinc salts of vanadium esters, in which slight increases in ORP have been observed compared to almost no decrease to very little decreases when calcium and potassium cations were in the formulation, respectively. These results were unusual considering the decrease in ORP values of the control solutions and the immersion solutions of other tested inhibitor compounds that had similar inhibition efficiencies. Qualitative analyses of the vanadium ester treated coupons revealed clear surfaces with no uniform corrosion except a few pits. In the IR spectra of coupons treated with vanadate esters, contained absorptions that might have been due to vanadium oxides in the low frequency region of 400 cm^{-1} to 1000 cm^{-1}, but these were not resolved sufficiently to deduce such a conclusion. Overall, the vanadates seemed to work similarly to chromates; however any conversion coating that might be formed is either not adherent to the substrate surface or not resistant to the cleaning solution of 50% hydrochloric acid. In agreement with the results for the vanadium esters, the ORP values of the immersion solutions of calcium and zinc gluconate salts did not decrease as opposed to magnesium and sodium gluconate salts, which showed significant decrease. The zinc salt had the lowest decrease of all of the gluconates. Since all gluconate salts had similar high inhibition efficiency values, the difference in ORP values is likely due to the cathodic inhibitive properties of zinc and calcium cations resulting in precipitation of zinc and calcium hydroxides at cathodic sites.

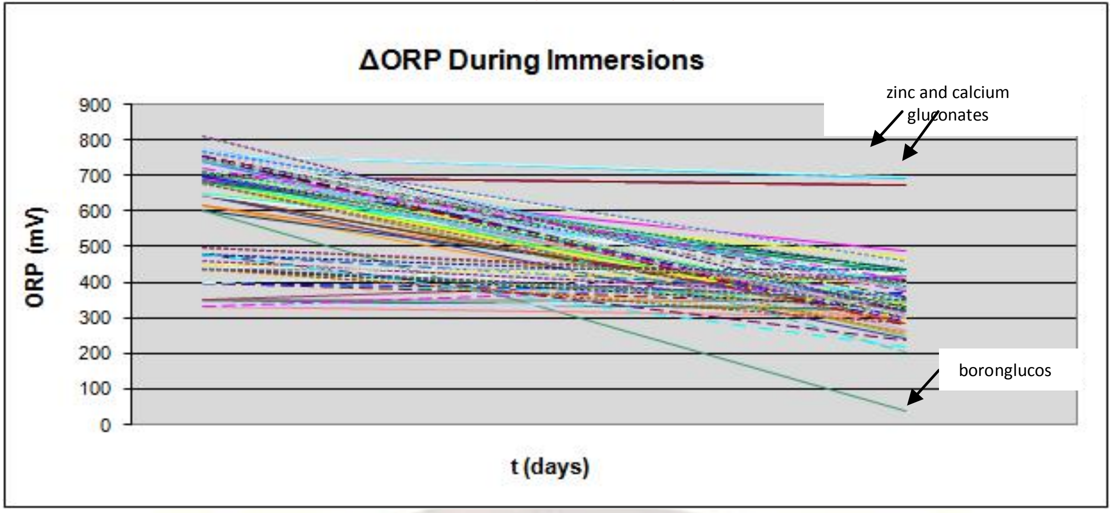

Figure 1 ORP (Oxidation-Reduction Potential) vs. Time Graph of Immersion Solutions of Various Inhibitors During Immersions of Coupons

Below ΔORP graph indicates the majority of corrosion inhibiting compounds' ORP values lowered by an average of roughly 350 mV.

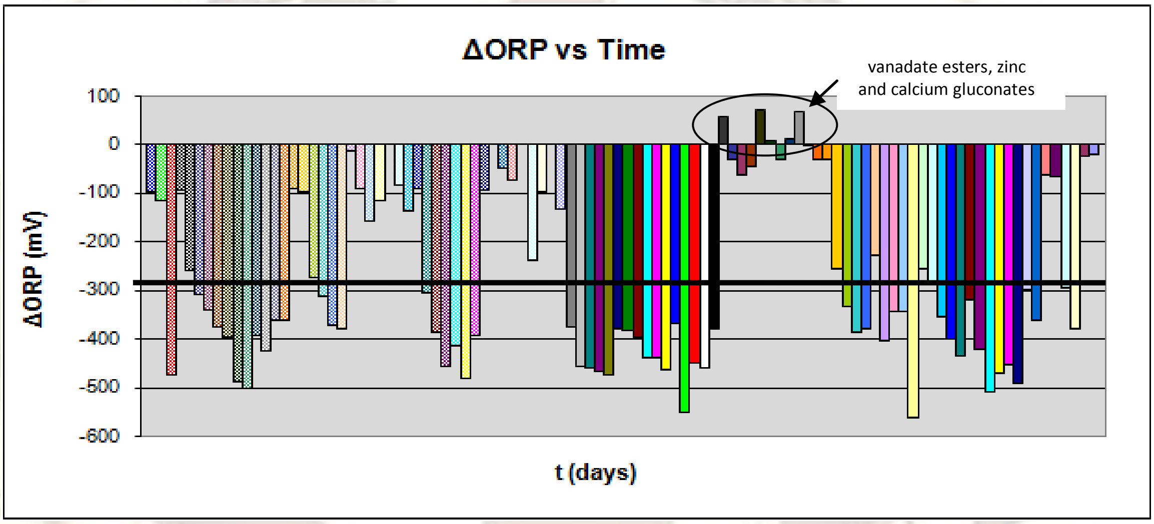

Figure 2 ΔORP vs. Time Graph of Immersion Solutions of Various Inhibitors During Immersions of Coupons

The ΔORP vs IE graph shown below indicates that the majority of the compounds that had ORP values decreased by an average of ~350 mV had positive inhibition efficiencies in the range of 50% to 100%.

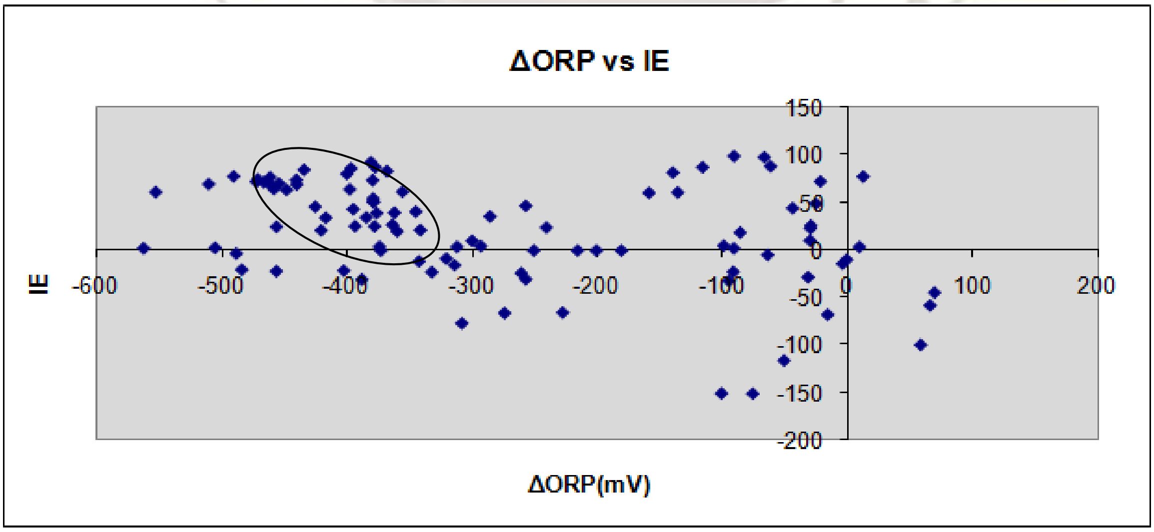

Figure Error! No text of specified style in document. ΔORP vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors

The ΔORP/ORP$_{initial}$ vs IE graph below indicates that the average ORP values were roughly halved for over 100 tested compounds with the exception of zinc and calcium gluconates and the vanadate esters.

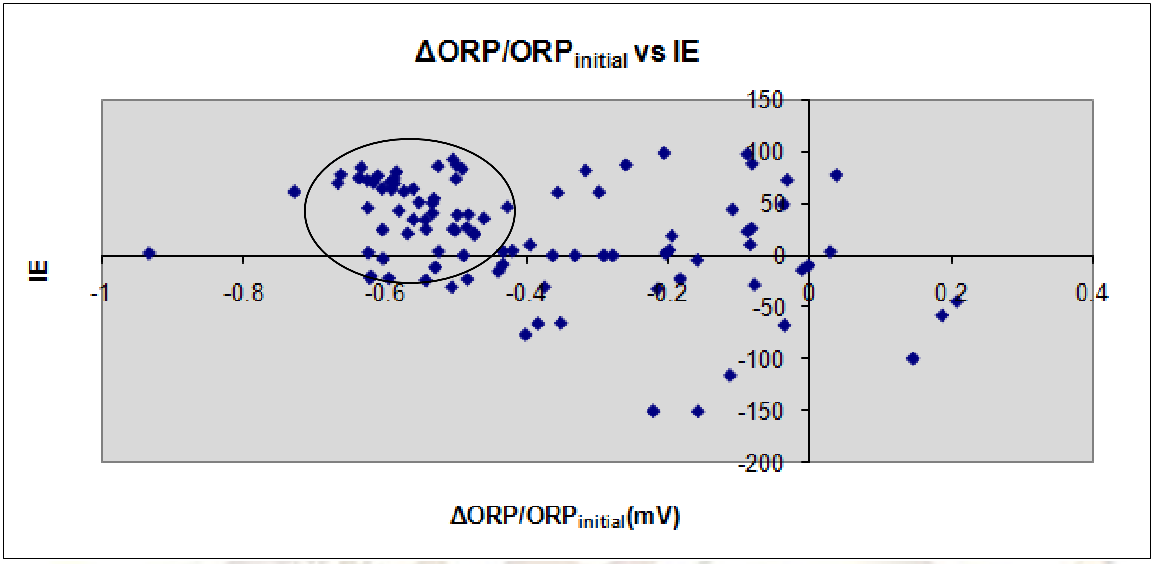

Figure 4 ΔORP/ORPinitial Ratios vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors

The vast majority of the ORP values were found to be within the range of 200 mV and 500 mV with the exceptions of the immersion solutions with various concentrations of calcium or zinc gluconate salts and the boroglucose solution which had an ORP value down from 600 mV to almost 0 mV.

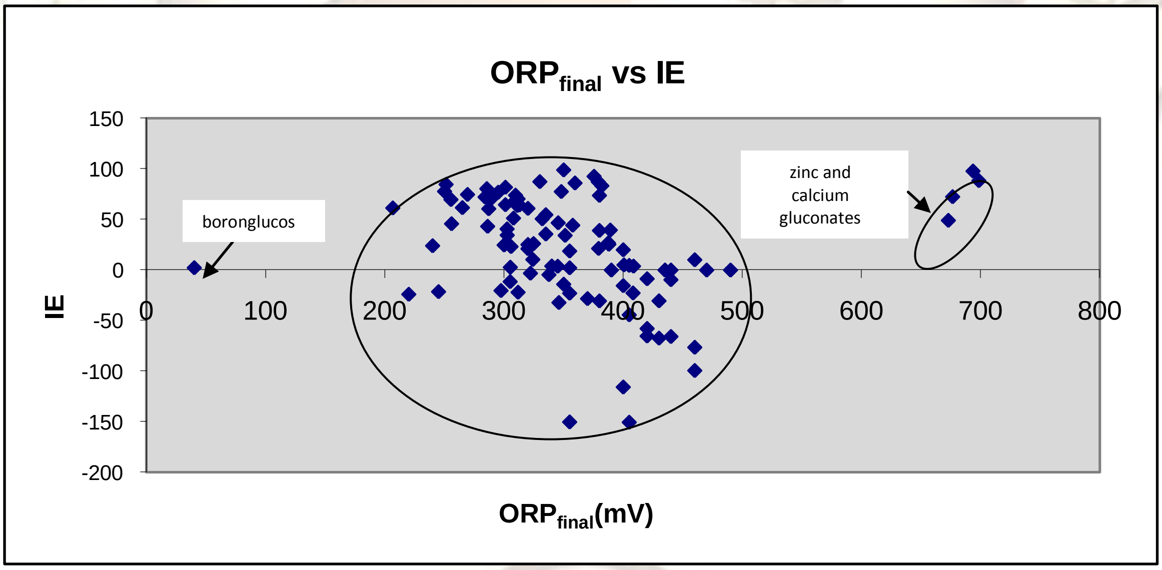

Figure 5 Final ORP Values vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors

2.2. PH GRAPHS

In acidic solutions an increase in pH occurs due to hydrogen evolution caused by the reduction of hydronium ions. In near neutral to basic solutions, the system chosen for this study, the pH also increases due to the anodic reaction of corrosion process, that is

$O_2 + 2H_2O + 4e^-$ $4OH^-$, $\longrightarrow$ (Eq. 1)

Accordingly, pH of the immersion solutions of good inhibitors increased only slightly, while a large increase was observed for compounds with poor corrosion inhibition ability. One week immersion solutions containing boroglucose, borogluconate, and the molybdenum esters of gluconate salts had higher ΔpH and final pH values than the other tested compounds. This is also correlated with the trends observed by ORP measurements.

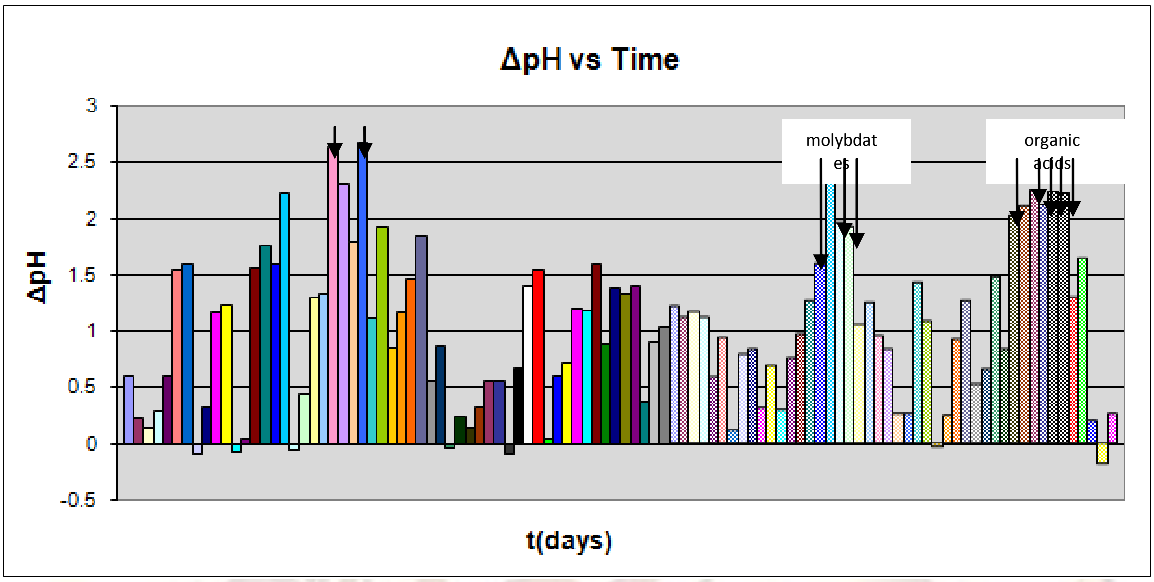

Figure 6 ΔpH vs. Time Graph of Immersion Solutions of Various Inhibitors During Immersions of Coupons

On the other hand, the gluconate salts and vanadium esters of gluconate salts had either very little increase or very little decrease in their pH values, again agreeing with the ORP measurements and inhibition efficiency results. Overall, the ΔpH values were within ~ -0.2 and 2.6. The final pH values vs IE and $\Delta pH/pH_{initial}$ values vs IE graphs did not reveal any other trends other than the aforementioned ones.

2.3. CONDUCTIVITY GRAPHS

The conductivities of the immersion solutions initially originated mainly from the initially present inhibitor concentration of 200 ppm and the 60 ppm chloride. However, as the corrosion and corrosion inhibition processes took place many other products contributed to the final conductivity values.

Most decreases in conductivity occurred for immersions of 10 and 14 day periods with no inhibitor present during the second immersion period. These results are in harmony with the inhibition efficiency results suggesting the total consumption of the inhibitors and precipitation of ions originated from corrosion reactions leading to a lower final conductivity. The exception to this trend was the immersion solution of the $Al(gluconate)_2OH$ treated coupon, which revealed a slight increase in conductivity in harmony with the inhibition efficiency results.

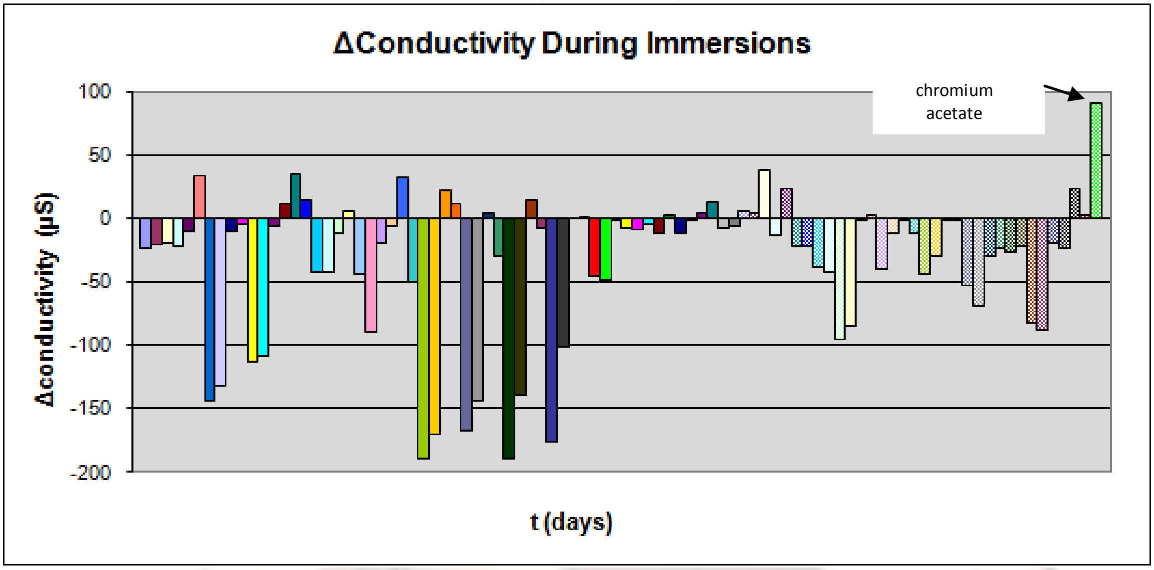

Figure 7 Δσ (Conductivity) vs. Time Graph of Immersion Solutions of Various Inhibitors during Immersions of Coupons

The immersion solutions with high inhibition efficiencies revealed no or slight positive increases in their conductivities. This included one week immersion solutions of gluonate salts and their esters in general. The immersion solution of chromium acetate revealed the only out of trend result with the highest increase in conductivity. Notably, the inhibition efficiency of chromium acetate treated mild steel coupon was also highly negative.

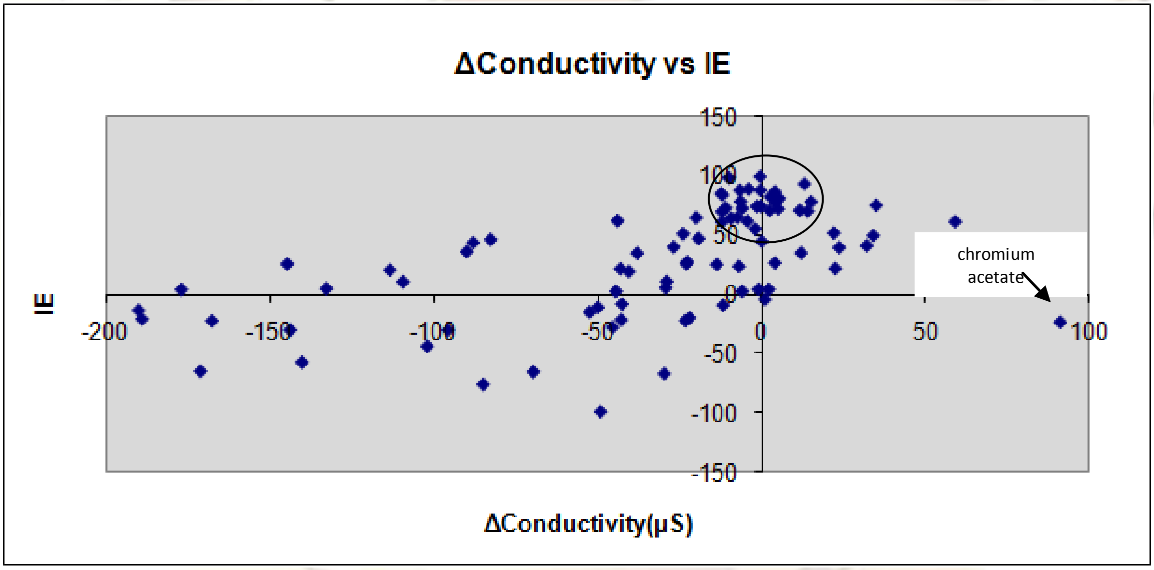

Figure 8 Δσ (Conductivity) vs. Inhibition Efficiency Graph of Immersion Solutions of Various Inhibitors

Most of the final conductivity values were within the range of 100 µS to 200 µS, close to the initial conductivity values. Plotting final conductivity values vs IE and Δconductivity/initial conductivity values vs IE did not reveal other trends but the aforementioned ones.

3. CONCLUSIONS

Oxidation-reduction potential, pH, and conductivity measurements of immersion solutions before and after completion of immersions revealed valuable characterization results supplementary to weight-loss test results. 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.

4. ACKNOWLEDGEMENTS

Assoc. Prof. Dr. Allen Apblett is acknowledged for the expertise and knowledge he provided me during my PhD education making it possible for me to proceed further in research and science. Also, Ishik University is acknowledged for the financial sponsorship provided for this project.

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