SYNERGY EFFECT OF CORROSION INHIBITORS FOR PROTECTION OF MILD STEEL IN COOLING WATER SYSTEM

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Abstract

The Cooling system in refining and petrochemical plants suffers from aqueous corrosion due to the direct contact between the metal and the aqueous solution which can be controlled by many methods. Corrosion inhibitors are the most used water treatments which are found in various types and added depending on the cooling system conditions; e.g. the presence of aggressive ions, working temperature, water movement, etc. Due to the high toxicity of chromate as an anodic corrosion inhibitors, they have been replaced by more friendly corrosion inhibitors such as molybdate which are considered relatively expensive, and inhibition is achieved at high concentrations, thus another inhibitor must be added (e.g. polyphosphate and/ or zinc-phosphonate) to afford the required inhibition with low concentrations of molybdates. In this study, two different inhibitors were used (sodium molybdate and zinc-phosphonate) individually and together in different concentrations. Sodium molybdate, Na_2MoO_4, a non-toxic anodic, environment-friendly corrosion inhibitor and zinc-phosphonate is a cathodic inhibitor which is also environment-friendly corrosion. The best performed inhibitor concentration with the use of sodium molybdate was 4000 ppm and 20 ppm with the use of zinc-phosphonate. When both inhibitors were used with different concentrations, the best inhibitor efficiency on the mild steel surface was achieved with 50 ppm Zn- phosphonate with 300 ppm sodium molybdate where it reached 96%.

Keywords*:* Corrosion inhibitor; Sodium molybdate; Zinc phosphonate; Mild steel.

الملخص

نظام التبريد في المصافي والمصانع البتروكيماوية تعاني من كترة التآكل وذلك بسبب الإتصال المباشر بين المعدن والمحاليل المائية، والذي يمكن التحكم في هذا التآكل بواسطة العديد من الطرق. إن موانع التآكل هي أكثر الطرق إستخداما في معالجة المياه وهى متوفرة بأنواع مختلفة، وتضاف هده الموانع بالإعتماد على ظروف نظام التبريد، مثل وجود الأيونات المسببة للتأكل, ودرجة حرارة التشغيل, وحركية الماء. وبسبب هده السمية العالية من للكرومات المستخدمة كمانع تآكل مصعدي فقد أستبدلت بموانع تآكل صديقة وغير ضارة، مثل المولبيدات التي تعتبر دات تكلفة عالية نسبيا وتحتاج إلى تراكيز عالية لمنع حدوث التآكل، لذا يجب أن يضاف مانع تأكل آخر مثل متعدد الفوسفات أو فوسفيت الزنك أو غيرها من موانع التآكل، بهدف الحصول على الحماية المطلوبة بتراكيز منخفضة للمولبيدات. وفى هذه الدراسة تم إستخدام نوعان مختلفان من موانع التآكل، وهما مولبيدات الصوديوم وفوسفيت الزنك، حيث تم إستخدام كل واحد منهما على حده، وكدلك أستخداما معاً بتراكيز مختلفة. حيث يعتبر مولبيدات الصوديوم Na_2MoO_4 هو مانع جيد للتآكل، أنودى وغير سام وصديق البيئة، وكدلك فوسفيت الزنك هو مانع للتآكل، كاثودي، وهو أيضا صديق للبيئة. إن أفضل تركيز لمانع التآكل باستخدام مولبيدات الصوديوم كان بتركيز 4000 ppm وبتركيز 20 ppm باستخدام فوسفيت الزنك، وعندما أستخدم هادين النوعان من موانع التآكل، وهما مولبيدات الصوديوم وفوسفيت الزنك بتراكيز مختلفة، وكانت أفضل كفاءة على سطح الصلب الحديدي (50 ppm من فوسفيت الزنك مع 300 ppm من مولبيدات الصوديوم) حيت وصلت الكفاءة الى 96%.

الكلمات المفتاحية: مثبط التآكل مولبيدات الصوديوم فوسفونات الزنك الفولاذ الطري

Introduction

Mild steel is widely applied as a construction material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost. Corrosion is the destruction or deterioration of metals. Corrosion in cooling water systems greatly affects the health of human beings and the economic level of the

world. One of the most practical methods for protection against the excessive dissolution of metal by corrosion is the use of proper inhibitors [1].

The use of corrosion inhibitors is one of the most common methods employed to enhance the corrosion resistance of metals. Generally, the inhibitor molecules are adsorbed on the metal surface leading to the formation of a protective film that restricts access of the corrosive environment to the metal surface. Corrosion inhibition of metals and alloys is of technical, economical, and environmental importance. Steel is the backbone of many industries. Corrosion inhibitors are commonly used to reduce corrosion attacks on the steel surface. The presence of the inhibitors leads to a decline in steel corrosion rate, increasing its lifetime [2-6].

Phosphonates have been extensively used as water treatment agents because of their low toxicity, high stability and corrosion inhibition activity in neutral aqueous media [7,8]. The reason for choosing phosphonate as an inhibitor is its property of adsorption on the metal surface, thereby forming poorly soluble compounds and thus decreasing the area of active metal surface or by an increase in the activation energy. Thus, the corrosion rate is decreased, which proves that corrosion in aqueous media is an electrochemical process. Phosphonates have high hydrolysis stability and they cannot be easily degraded by microorganisms. In phosphonate-based inhibitor system, the inhibition efficiency was increased by the addition of metal cations like Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, Fe^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+}. etc., in nearly neutral media. In the above series, zinc was chosen as the good metal ion to enhance the inhibition property of phosphonates [9,10].

The cost of inorganic inhibitors is low, but most are toxic e.g., chromate, mercuride, nitrite, arsenate, etc. [11]. As an environmentally acceptable and effective corrosion inhibitor for zinc, galvanized steel, and other metals, molybdate ion (MoO_4^{2}) has been widely investigated in a variety of corrosive media [12-14]. Many other researchers have concentrated on the synergetic effect

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between molybdate ions and other organic and inorganic compounds for corrosion reduction in cooling water systems [15,16]. Different operational parameters such as cooling water pH, inhibitor concentration, water circulation velocity and the concentration of the other ions present in water may have a considerable influence on molybdate inhibition efficiency in cooling waters [17,18]. Natural water is frequently used in cooling systems. This use needs in especially cases treatments to minimize the corrosion of processes metals. Open recirculating cooling water systems that reuse cooling water are frequently used at large central utility stations, chemical, petrochemical, and petroleum refining plants, steel and paper mills, and all types of processing plants [19].

The primary objectives of cooling water treatment are to maintain the operating efficiency of the cooling water system and to protect the equipment that contacts the cooling water. These objectives are accomplished by controlling or minimizing deposition, corrosion, and microbiological growth on the cooling water equipment. The deposits that occur in cooling water systems are usually divided into two categories: scale and fouling. The presence of either type of deposit in the heat exchangers or in the film fill can interfere with heat transfer, thereby reducing the efficiency of operation. Deposits can also promote under-deposit corrosion [20]. The objective of the present research was to investigate corrosion inhibition by MoO_4^{-2} with and without the presence of zinc phosphonate on mild steel surface under different concentrations of both inhibitors. Experimental work was carried out in distilled water as an electrolyte and in an aerated system where different concentrations of each inhibitor (sodium molybdate and zinc phosphonate) were tested individually and together. Measurements were applied using electrochemical techniques, potentiodynamic and potentiostatic techniques. Also, open circuit potential (OCP) of mild steel was measured as a function of time which is known as the potential/ time curves.

2. Experimental Work

2.1 Specimens Preparation

Samples used for experiments containing only one metal (i.e. mild steel) in the solution were cut into a square shape with a surface area of 1 cm^2. These samples were welded to a conductive wire and cold mounted in metallographic epoxy resin. For each experiment, the exposed face was ground using Si/C paper of 600 grit prior to being washed with deionized water and dried.

2.2 Solution Preparation

In this research, experiments were carried out in blank solutions and those containing one type of inhibitor. Two types of inhibitors were tested, sodium molybdate (Na$_2$MO$_4$), and zinc-phosphonate with different concentrations of each. The synergetic effect of the two inhibitors was also tested with different concentrations.

2.3 Preparation of Inhibitor-Containing Solutions

A stock solution of 5000 ppm was prepared of each inhibitor. The required concentration of each inhibitor was prepared by the dilution of the stock solution to the needed concentration. Test concentrations of inhibitors differed from one inhibitor to the other depending on the concentration need, thus not all inhibitors were studied at the same concentration.

2.4 Electrochemical Test Cell

The test container used throughout this work consisted of a Pyrex glass vessel which contained the metal specimen, commonly called the working electrode, immersed in the test solution. The working electrode was mild steel. A saturated calomel electrode (SCE) was used as reference electrode and a platinum electrode used as a counter electrode. Figure 1 shows electrochemical test cell.
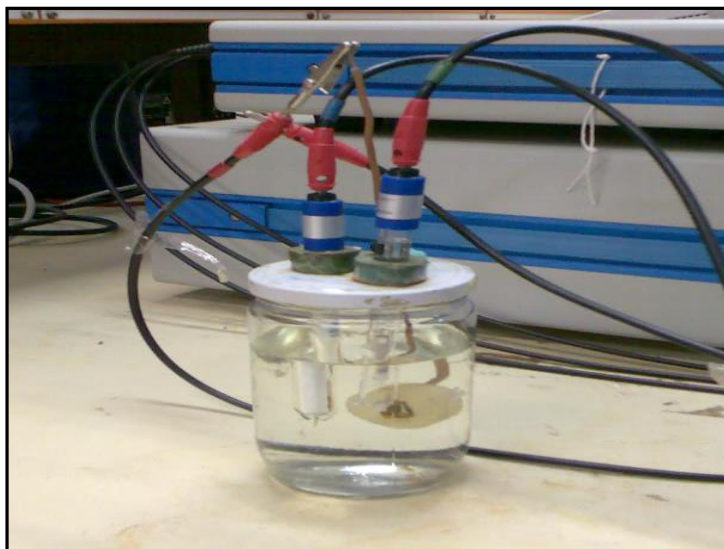
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Figure1: Electrochemical Cell

2.5 Electrochemical Measurements

The electrochemical tests that were carried out in this study are the potentiostatic and potentiodynamic techniques. Also, the potential change with time was applied (Potential –Time curves).

Figure 2: Potentiostatic technique

In all cases, the polarization curves were used to determine the corrosion current densities. Hence, the inhibitor effectiveness, from Tafel extrapolation of the anodic and cathodic regions of the curves to E_{corr}. On the other hand, the potentiostatic curves were used to determine the current outcome. Figure 2 shows Potentiostatic technique.

The Potential–Time Curves was applied for 15 minutes from the emersion of the working electrode into the solution. By this test we can determine the change of potential with time. After the end of the potential measurements, the potentiostatic technique was carried out by measuring the current with time. The test was applied for 15 minutes. The used mild carbon steel was tested under the use of potentiodynamic technique. The metal was left for 30 minutes. So that, the E_{Corr} would stabilize and then connected to the potentiostatic and set to scan from -250 mV of the E_{Corr} to +250 mV of the E_{Corr} with a scan rate of 0.1667 mV/sec. The results were plotted between a potential vs. current density.

2.6 Effect of Inhibitor Concentration

The most effective concentrations of the individual two inhibitors were selected for further testing. These tests were applied on mild steel where they were carried out by using potentiodynamic technique, potentiostatic technique and potential change with time at room temperature ($22 \pm 1°C$). Sodium molybdate was tested at concentrations of 100, 300, 400, 600, 800, 1000, 1400, 2000 and 3000 ppm; zinc phosphonate was tested at concentrations of 10, 20, 25, 30, 50, 60 and 80 ppm. The concentrations of mixed inhibitors were 10 ppm zinc phosphonate with 600 and 1400 ppm Na_2MoO_4 individually. 20 ppm zinc- phosphonate with 50 Na_2MoO_4. 100 ppm Na_2MoO_4 with 20, 30 and 50 ppm zinc phosphonate. 300 ppm Na_2MoO_4 with 5, 10, 15, 30 and 50 ppm zinc- phosphonate.

3. Results and discussion

The performances of the two inhibitors (Sodium molybdate and zinc- phosphonate) were tested under different concentrations to achieve the optimum concentration. The two inhibitors were also

tested by the mixture of both in different concentrations. The electrochemical techniques used in this study were potentiostatic, potentiodynamic and a measurement of potential- time curves. All tests were carried out at room temperature.

3.1. Effect of concentration on the performance of sodium molybdate

The performance of Na_2MoO_4 on mild steel is shown in Figures (3), (4), and (5). Results achieved by using the potentiodynamic technique. Figure (3) shows that the protection was achieved with an inhibitor concentration of best 4000ppm were the corrosion current density was $1*10^{-6}$ A\cm^2 and a corrosion rate of (0.041) mpy was recorded. The inhibitor efficiency with use of this concentration was (87.5%) which indicates that a very good protection. This high inhibitor efficiency was achieved due to the presence of both oxygen and molybdate in the aerated solution which were adsorbed at the metal surface and oxygen was the main passivator where it produced a passive oxide film on mild steel. The adsorbed molybdate initially formed a ferrous molybdate which is transformed via oxidation to ferric molybdate. The ferric molybdate provided a blocking effect as well as repairing the passive oxide film. The adsorption of molybdate blocks the outward diffusion of ferrous ions.

As the inhibitor concentration decreased the corrosion rate increased, where a corrosion rate of 0.02 mpy was recorded with an inhibitor concentration of 3000 ppm. With the use of 100 ppm a higher corrosion rate was recorded $1.62*10^{-7}$ mpy. This is related to the unprotected areas on the mild steel surface where the protective film was not fully formed on the entire surface.

Figure (4) shows test results achieved with the use of potentiostatic technique. The Figure indicates the change of current with time where with all inhibitor concentrations there was a decrease in current with time which indicates that there an film forming in the metal surface that blokes the lowest current value was recorded with the use of an inhibitor concentration of 4000 ppm which confirms with the result that were achieved by the potentiodynamic technique.
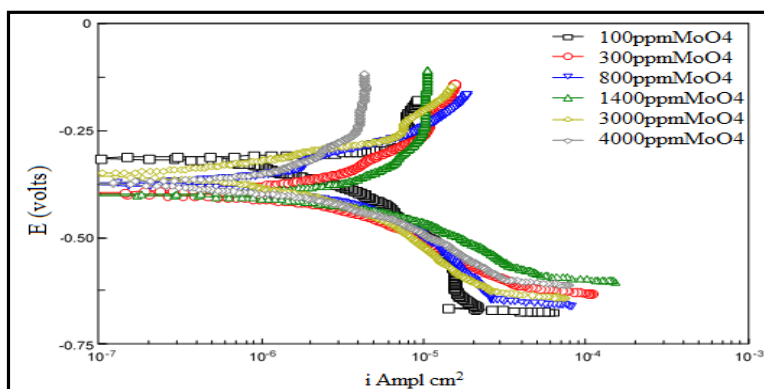
Figure (3) Polarization curves for different concentrations of sodium molybdate.

Figure (4) shows test results achieved with the use of potentiostatic technique. The Figure indicates the change of current with time where with all inhibitor concentrations there was a decrease in current with time which indicates that there an film forming in the metal surface that blokes the lowest current value was recorded with the use of an inhibitor concentration of 4000 ppm which confirms with the result that were achieved by the potentiodynamic technique. Even though, there was a variation in the current value achieved by each inhibitor, there was only a slight difference in the current values except for 4000 ppm where the current value was $3*10^{-6}$. However, they are within the range of 1 to $2*10^{-6}$.
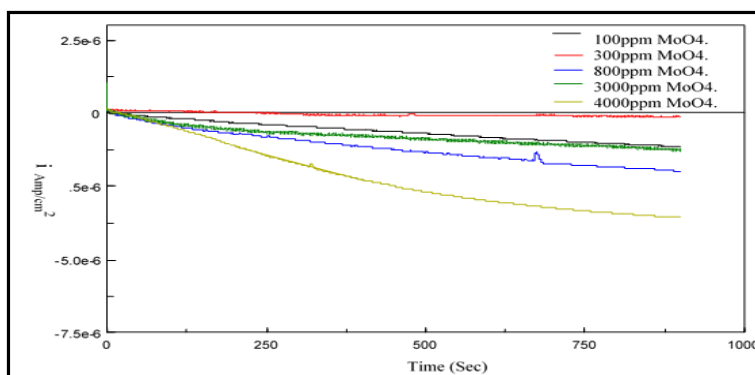

Figure (4) Potentiostatic curves for different concentrations of sodium molybdate.

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Potential –Time curves also show that the best performed inhibitor concentration was 4000 ppm this is estimated from the potential decrease to the positive side with time. This indicates that the achieved protection did not change very significantly with concentration. As the inhibitor concentration increased the E_{corr} shifted in the positive (noble) direction as shown in Figure (5).
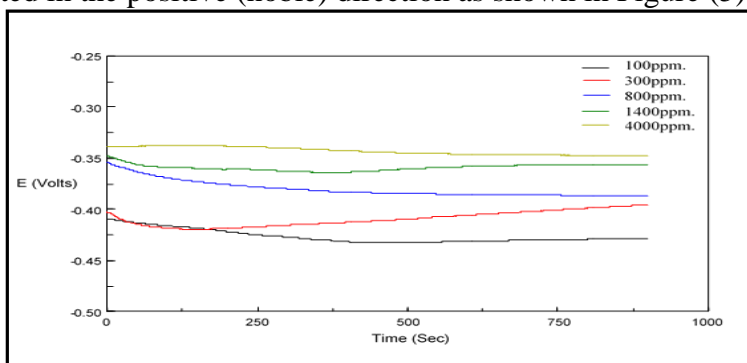
Figure (5) Potentiostatic curves for different concentrations of sodium molybdate.

3.2. Effect of concentration on the performance of zinc phosphonate

Figure (6) shows the effect of concentration on the inhibition of mild steel surface provided by zinc phosphonate corrosion inhibitor. As the Figure shows, the best achieved concentration was 20 ppm with a corrosion rate of (8.10×10^{-8}) mpy and an inhibitor efficiency of (75%). due to the cathodic protection that was provided by using zinc-phosphonate where the zinc effectively counteracts the anodic character of the phosphonate through the formation of zinc-phosphonate complex. The protective film that was formed by zinc and phosphonate consisted of two layers. The top layer consisted of zinc as hydroxide, the bottom layer consisted of iron oxide and zinc phosphonate complex. With the use of lower concentration (10 and 15 ppm) there was a decrease in the inhibition and a corrosion rate $1.21*10^{-7}$, $3.24*10^{-7}$ was recorded respectively. This can be attributed to the incomplete coverage of the metal surface with the protective film. There was also an inhibition decrease as the inhibitor concentration increased above 20 ppm (30 and 50 ppm)

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and a rise to the corrosion rate $8.10*10^{-8}$, $1.63*10^{-7}$, $1.21*10^{-7}$ respectively due to the formation of a soluble iron phosphonate complex film on the metal surface.
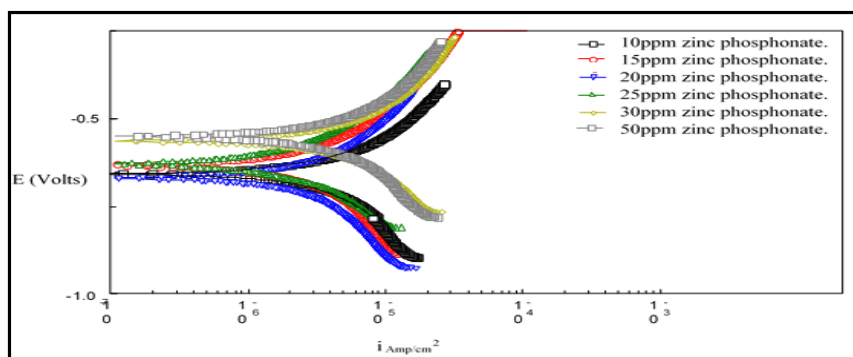

Figure (6) Polarization curves of different zinc phosphonate concentration

Potentiostatic results shows the change of current with time. The lest current value achieved was with the use of 20 ppm where on the steel surface, phosphonates coordinated with Fe^{2+} to form Fe^{2+} phosphate complex on the metal surface. In general, increase in inhibitor concentration led to a current decrease with time. This is illustrated in Figure (7), it was due to the heterocyclic compounds, thus phosphonate that formed an insoluble complex with the zinc on the metal surface in the aqueous solution which provided a protective film.
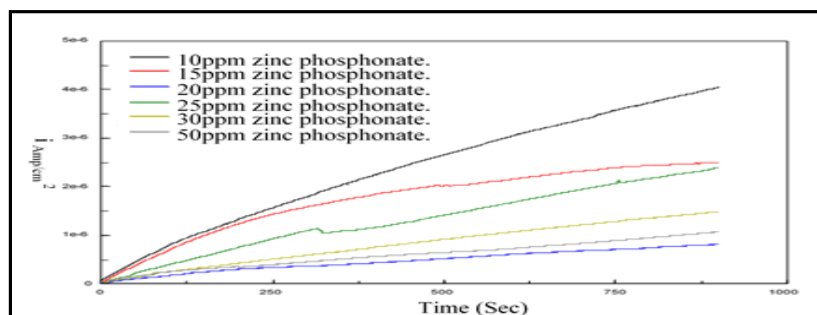

Figure (7) Potentiostatic curves for different concentrations of zinc phosphonate.

Zinc phosphonate worked as a cathodic inhibitor that formed a barrier between the metal surface and the bulk solution which in return prevented the oxygen diffusion to the metal surface and the potential of the metal remains fairly negative. As the Figure (8) shows the best achieved concentration was 20 ppm which gave the most negative corrosion potential. Thus other concentrations gave a more positive potential. All results achieved by potentiodynamic and potentiostatic techniques and also potential –Time curves indicated that the best performed inhibitor concentration was 20 ppm of zinc phosphonate.
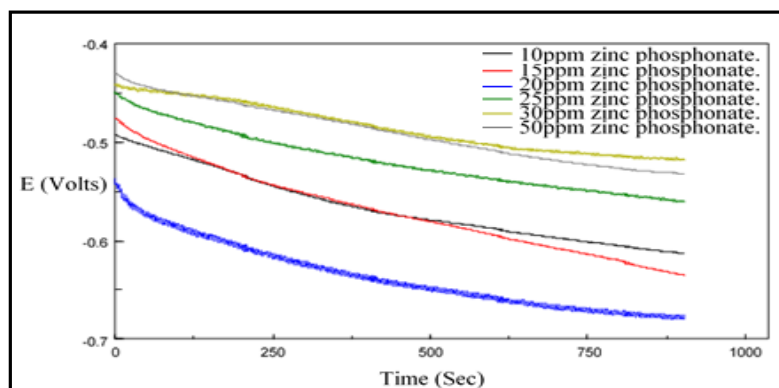

Figure (8) Potential- Time curves for different concentrations of zinc phosphonate

3.3. Effect of inhibitor mixture on the inhibition of mild steel

The effect of mixing both inhibitors (zinc phosphonate and sodium molybdate) led to a higher efficiency even with the use of lower concentrations than those required to give protection when both inhibitors were use individually. This can be observed from Figure (9) where with the use of a mixed inhibitor of 20 ppm zinc phosphonate and 300 ppm sodium molybdate, the corrosion current density decreased and passivity was achieved even though when both inhibitors were used individually and with the same concentration, a higher corrosion current density was recorded. As shown in Figure (9) there was a potential shift towards the positive site (anodic site) with the used of mixed inhibitors which indicates

that the more dominate inhibitor was sodium molybdate been the anodic inhibitor.
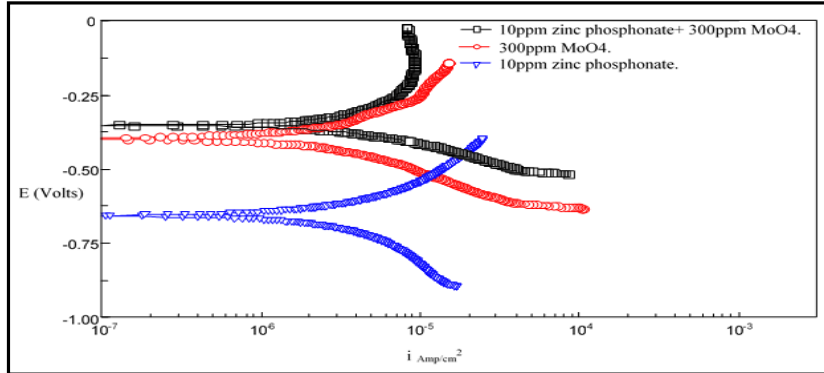

Figure (9) Polarization curves for 20 ppm zinc phosphonate and 300 ppm sodium molybdate mixed and individual.

However, when a concentration of 20 ppm zinc phosphonate and 100 ppm sodium molybdate were used a good protection was achieved. There was a potential shift towards the positive site compared with 20 ppm zinc phosphonate alone but the potential was more negative to the 100 ppm sodium molybdate which indicates that both inhibitors worked on the metal surface at the same time and protection was achieved on the cathodic and anodic sites as well. The protection was due to the formation of iron molybdate complex on the anodic sites and zinc phosphonate complex on the cathodic site.
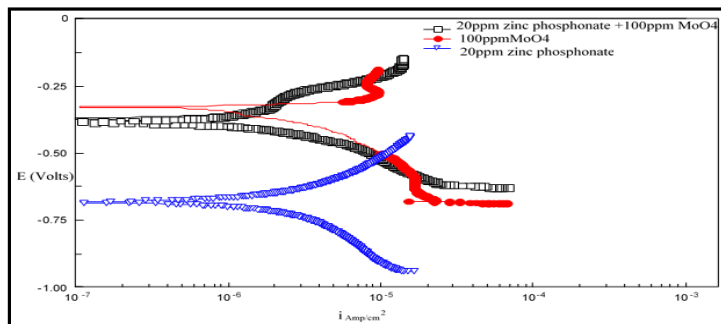

Figure (10) Polarization curves for 20 ppm zinc phosphonate and 100 ppm sodium molybdate individually and mixed.

Figure (11) shows the There was almost no change to the corrosion current density and also to the corrosion potential (E_{corr}) which indicates that the addition of 10 ppm zinc phosphonate had almost no effect on the performance of 1400 ppm sodium molybdate due to the low concentration of zinc phosphonate (10 ppm) and relatively high concentration of sodium molybdate.
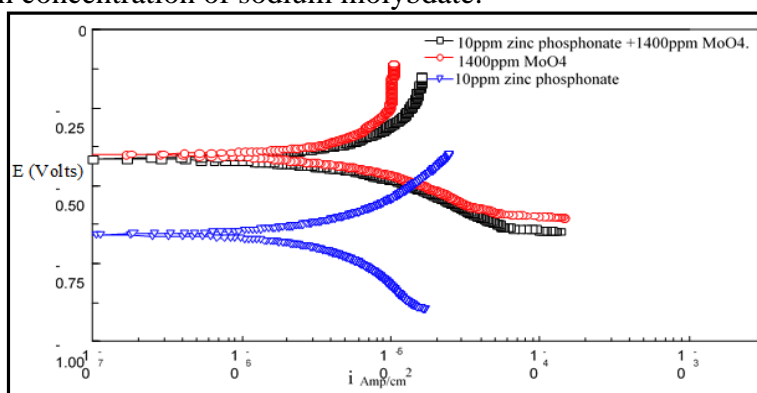

Figure (11) Polarization curves for 10 ppm zinc phosphonate and 1400 ppm sodium molybdate, mixed and individually.

Figure (12) shows the effect of addition of different concentrations of zinc phosphonate to 300 ppm sodium molybdate. As it is shown the best performed concentration was with the highest concentration of zinc phosphonate (50 ppm).
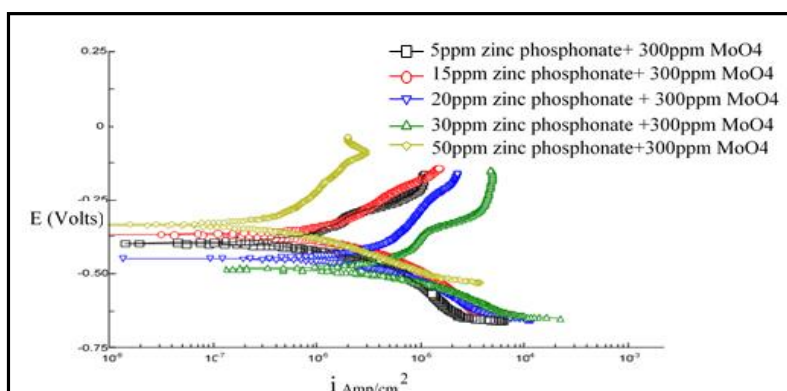

Figure (12) Polarization curves for different concentrations of zinc phosphonate with 300 ppm sodium molybdate.

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4. Conclusion

In this research, Sodium molybdate being an anodic inhibitor where a shift to the corrosion potential towards the positive site. Best inhibition concentration of sodium molybdate is 4000ppm where the recorded corrosion rate was $4.05*10^{-8}$. Results achieved by potentiodynamic technique confirm with those obtained with potentiostatic technique that best sodium molybdate concentration is 4000 ppm. Optimum inhibitor concentration of zinc phosphonate is 20 ppm. The addition of zinc phosphonate and sodium molybdate improved the inhibition of both inhibitors when used individually even at low concentrations of sodium molybdate (300 ppm) that gave low protection when used alone.

Acknowledgements

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