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CORROSION INHIBITION OF METHIONINE AS A GREEN CORROSION INHIBITOR FOR CARBON STEEL IN THE PRESENCE OF METHANOL AND MONOETHANOLAMINE

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Abstract - The study of carbon steel corrosion is paramount in many industries as corrosion of metal surfaces incurs massive losses to the industries. Numerous authors worked on corrosion inhibitors but the results shown by the amino acids are promising. Due to this fact, the corrosion rate of aqueous methionine solvents against carbon steel with the weight-loss method was studied in this work. In this weight-loss method, the metal specimens were dipped in aqueous methionine solvents for a specified time. After the exposure, values were put into the formula for calculating results. The results showed that without using the aqueous methionine solution, the corrosion of carbon steel was 2.41 mm/year. For a lower methionine concentration solution (2% MTH, 8% Methanol, and 20% MEA), the corrosion against carbon steel dropped to 0.85 mm/year with a protection efficiency of 62.40%. For a medium concentration solution (5% MTH, 5% Methanol, and 20% MEA), the corrosion reached 0.82 mm/year with a protection efficiency of 63.77%. But as the concentration of methionine was increased, it was found that the corrosion also increased greatly, because, at a higher concentration of methionine (8% MTH, 2% Methanol, and 20% MEA), corrosion became 0.76 mm/year with a protection efficiency of about 66.81%. The presence of methionine lowers the corrosion rate even much better than other amino acids. The inhibition efficiencies of methionine are augmented with improved methionine concentration. The new solvent mix can be employed as an efficient corrosion inhibitor.

Keywords - Corrosion, Carbon Steel, MTH (Methionine), Amino Acids, Methanol, MEA (Monoethanolamine), Weight Loss Method.

I. INTRODUCTION

The carbon steel corrosion is the talk of the town as huge losses are incurred due to it. Carbon steel has a number of applications in buildings and bridges, cars, gears, rails, pipelines, axles, fridges, and washing machines to name a few. Carbon steel alloys are mainly used in automobile body components, structural shapes, construction tools, machinery, forgings, tubing, wiring, etc. It is also a known fact that carbon steel alloys are able to handle corrosion more effectively as compared to ordinary steel. But it is not better than stainless steel because it does not have corrosion-resistant properties like that of stainless steel. Being more solid and durable, still it erodes faster than stainless steel if exposed to moisture. Carbon steel is prone to corrosion if the relative humidity of the atmosphere is 70% - 80% and the atmosphere heat is more than 32 F. To solve this issue, aqueous methionine solutions would be used as green corrosion inhibitors.

Nowadays, corrosion inhibitors are utilized all around the world to protect metal and alloys in corrosive environments. But as these toxic inhibitors are useful, they also come with a number of drawbacks like they are hazardous to health in addition to being highly toxic. Due to this fact, only green corrosion inhibitors are most recommended for corrosion prevention. Although many green non-organic compounds are used before as corrosion inhibitors, they have not been successful at elevated temperatures. To deal with this issue, amino acids are perfect when it comes to green corrosion inhibitors. As these amine-based absorption processes are utilized, these processes encounter serious corrosion problems. Almost one-fourth of the budget is specially allocated for corrosion prevention as this is a major problem.

As these amine-based corrosion inhibitors are green. These are also economical in terms of cost. In addition to that, they are biodegradable and even soluble in aqueous conditions. In numbers, there are at least 20 different amino acids, which are capable of forming proteins. As they have heteroatoms and π-electron in their respective molecules, being the cause of their utilization as green corrosion inhibitors. Myriad research papers prove this as the number of amino acids used as green corrosion inhibitors at various scales.

For this study, the one amino acid that is taken for observation is methionine (MTH). Methionine has both ($-NH_2$) and ($-S-CH_3$) groups. It is biodegradable and is a bit cheaper than other amino acids. Due to the sulfur atom inside the MTH, the inhibition efficiency increases.

Although various tests have been conducted on methionine in different solutions to check its corrosion inhibition, it has never been tested in aqueous methionine solutions before. These aqueous methionine solutions consist of monoethanolamine, methanol, and methionine in different compositions. For this study, the varied mass fractions of the aqueous methionine mixtures were as follows: 2% Methionine + 8% Methanol + 20% Monoethanolamine; 5% Methionine + 5% Methanol

+ 20% Monoethanolamine; and 8% Methionine + 2% Methanol + 20% Monoethanolamine.

The goal of this study was to seek a green corrosion inhibitor. This green corrosion inhibitor needs to be present commercially. In addition to that, it is economical for small-scale industries. This inhibitor is able to prevent carbon steel corrosion in carbon dioxide absorption processes where amino acids are used. The experimental technique utilized in this work is a simple weight loss technique.

II. RESEARCH METHODOLOGY

The study of carbon steel corrosion is paramount in many industries as corrosion of metal surfaces incurs massive losses to the industries annually. Numerous authors have worked on corrosion inhibitors but the results shown by the amino acids are promising. Due to this fact, the corrosion rate of methionine against carbon steel is studied in this work. The corrosion rate of aqueous methionine solutions is carried out with the help of the weight loss method. It is the simplest form of corrosion monitoring. The weight loss method basically means using a sample specimen in a corrosive condition for a limited amount of time and then finding out the change in weight with respect to time. The weight loss method is simple and quite straightforward as it has no special needs, it just needs any shaped coupon, a coupon holder, a blue cap bottle, nylon wire, a glass hook, and varying degrees of sandpapers. It is one of the oldest techniques yet still reliable in many circumstances. It is also widely used because it is simple (no complex equipment required), direct (direct measurement is easily attained), and versatile (possible in all corrosive conditions). As our research accepts averaged data and waits for the slow response, this weight loss method is ideal in these circumstances.

Several chemicals were purchased for the current research. Chemicals like Methionine (≥97% pure), sodium hydroxide (≥99% pure), and monoethanolamine (≥99% pure) were purchased from the chemicals hub, Karachi, Pakistan. These chemicals were not further purified. In order to make the solvent blend, the aqueous blend of Methionine was required, so it was made by neutralizing Methionine dissolved in the double distilled water, with NaOH of equimolar amount. In this aqueous solution, no other component was added so far. For all kinds of measurements of weight, an electronic balance was utilized with a precision of $\pm 1\cdot10^{-5}$ g. Various mass fractions of Methionine blends were 2% MTH + 8% Methanol + 20% MEA, 5% MTH + 5% Methanol + 20% MEA and 8% MTH + 2% Methanol + 20% MEA. This range of concentration of Methionine is chosen as per the commercial usage of solvent in the carbon dioxide capture process.

Preparation of these coupons is the first step. This is a critical step as the choice of the method adopted for cleaning is crucial in attaining useful data. More the care is taken, the better the results would be. A number of surface finish methods are there for the desired use. This cleaning of carbon steel coupons before and after weighing is the most important step in making sure all contaminants are removed which can hamper the accurate results. To make sure the carbon steel coupons are cleaned properly, use of varying degrees of sandpapers like 150,300,500 grits were utilized for this purpose, and coupon preparation and cleaning were done as per the standards of ASTM G-1-90. No matter how much care is taken during the coupon preparation process, numerous uncontrollable factors like microstructural defects hamper the accuracy of results. To cope with this issue, coupon position and orientation come in handy. As the orientation parallel to flow is recommended by many researchers, therefore, this was also our preference. In addition to this, positioning is also important in attaining accurate results. For the most accurate results, when the carbon steel strip coupon is inside the vessel where the corrosion solvent is present and is fully submerged in it, the coupon can experience the same flow regime at all parts. After the coupon positioning and orientation, comes the coupon holder's part as the style and configuration of coupons are also important factors in deciding a coupon.

For this research, a fixed coupon holder was used with a size of 3 inches. For this experiment, all three different composition mixed solvents are taken into account for this corrosion experiment. Coupons used in this experiment are of carbon steel which has a density of 7.84 g/cm^3. To find the corrosion rate, these three metal specimens were hung with a glass hook in different corrosion solvents. Before starting the process, coupons were prepared as per the standards of ASTM G-1-90. After properly cleaning the metal specimens with varying sandpapers, the length and the breadth of the metal specimen were measured with the help of the vernier caliper, while the thickness of the metal specimen was calculated by screw gauge. After getting the dimensions of metal specimens for the area, their raw weight was calculated before the corrosion. After that, with a glass hook, the metal specimens were dipped in respective mixed solvent blends for a specified time. For the exposure part, aqueous methionine solvent is filled in a blue cap bottle of about 250 ml and the coupons are hung with respective coupon holders. Once the exposure is done, starts the post-exposure cleaning process which is quite similar to the coupon cleaning process as explained above. As the corrosion time was completed, the metal specimens were washed with tap water and cleaned with filter paper. To save metal specimens from reacting with water due to humidity, the metal specimens were put into a closed jar for about 30 minutes. Again, the weight of the metal specimens was calculated after the corrosion exposure. As all the values required for the formula of corrosion rate are attained. They are put into the formula for the results:

Corrosion rate = $\Delta W.K/A.t.\rho$ (1)

where ΔW is the weight loss in a metal specimen (grams), K is the constant for unit conversion, A is the area of the metal specimen (cm^2), and t is the exposure time of the metal specimen in mixed solvent blends (hours), ρ is the density of the metal specimen (gm/cm^3).

In order to get the best possible corrosion results, it is important to ensure that it has no localized corrosion. Across the carbon steel coupons, penetration is the same. The area of the carbon steel coupons is not changed while it was exposed to the corrosive environment.

The weight loss method was used because it had myriad benefits. Such as the cost incurred for the weight loss method is quite low. The entire corrosion process becomes simple and quite straightforward. This weight loss method can be used to for all conditions (solids, liquids, gases). The performance of aqueous methionine solvent as a green corrosion inhibitor can be easily assessed. With the help of the weight loss method, even the localized corrosion can be found out and calculated accordingly. Corrosion deposits and even visual inspection can also be understood and evaluated with the help of the weight loss method. These advantages make the weight loss method the most beneficial method for corrosion monitoring. As there are several advantages of the weight loss method as compared to other methods, there are also a few drawbacks. Elongated exposure periods are sometimes needed to get accurate results. The weight loss method only identifies the average rate of metal loss in an exposure time period. The carbon steel coupons cannot be reused and are not recommended for corrosion analysis. These were some of the drawbacks of the weight loss method for corrosion monitoring.

III. RESULTS AND DISCUSSIONS

Determination of corrosion rate is carried out with the help of the weight loss method. The results present in Table 1 show that without using the methionine, the corrosion of carbon steel was about 2.41 mm/year and had a protection efficiency of about 0%. For a lower concentration of aqueous methionine solution which is 2% MTH, 8% Methanol, and 20% MEA, the corrosion against carbon steel was reduced to 0.85 mm/year with a protection efficiency of about 62.40%. For the medium concentration of aqueous methionine solution which is 5% MTH, 5% Methanol, and 20% MEA, the corrosion was further reduced to 0.82 mm/year with a protection efficiency of about 63.77%. But as the concentration of methionine was increased, even more, it was found that the corrosion also increased greatly, because, at a higher concentration of aqueous methionine solution which is 8% MTH, 2% Methanol, and 20% MEA, corrosion became 0.76 mm/year with a protection efficiency of about 66.81%. This proves that the higher the quantity of methionine lower the corrosion rate would be. The inhibition efficiencies of methionine enhance with augmented methionine concentration. Methionine was able to give 66.81% inhibition efficiencies for carbon steel with a higher concentration solution (8% MTH, 2% Methanol, and 20% MEA).

The protection efficiency or inhibition efficiency (%) is calculated using equation (2):

Protection Efficiency (%) = [(CR uninhibited - CR inhibited) / CR uninhibited] x 100% (2)

where CR uninhibited is Corrosion Rate Uninhibited (without aqueous methionine solution) and CR inhibited is Corrosion Rate Inhibited (with aqueous methionine solution)

Conc. of Methionine	Carbon Steel mm/year	Protection Efficiency %
Blank	2.31	0
2% MTH + 8% Methanol + 20% MEA	0.85	62.40%
5% MTH + 5% Methanol + 20% MEA	0.82	63.77%
8% MTH + 2% Methanol + 20% MEA	0.76	66.81%

Table 1
Corrosion rate and Protection efficiency of aqueous Methionine solvents against Carbon Steel in mm/year, with and without inhibitor

It is quite evident here that as the quantity of methionine increased in the aqueous methionine solutions, the corrosion rate decreased. This shows the reaction of adsorption of corrosion inhibitor molecules on the carbon steel strip coupon's surface. In addition to that, as the quantity of methionine increased in the aqueous methionine solutions, the protection efficiency also started augmenting which shows they have a directly proportional relation. It is also found from the data, that without using any aqueous methionine solution, the corrosion rate is almost thrice as compared to any aqueous methionine solution.

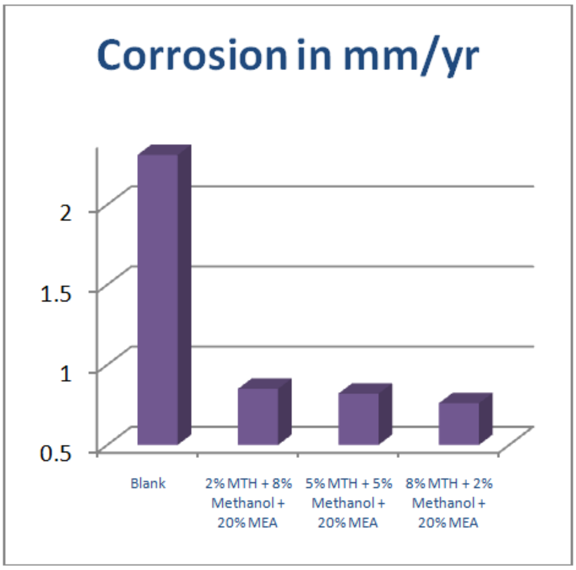

Figure 1: Corrosion rate for carbon steel in aqueous methionine solutions, with and without inhibitor

This is evident in Figure 1 which shows the corrosion rate for carbon steel in aqueous methionine solutions, with and without inhibitor, and also validates the above-mentioned result that with the presence of methionine inhibitor, the corrosion rate reduces because of the adsorption of amino acids on the carbon steel metal surface. It is because of the availability of R-S-R in the molecular structure of methionine that makes methionine a better candidate as compared to other amino acids. R-S-R in molecular structure is the main reason behind its enhancement of inhibition efficiency.

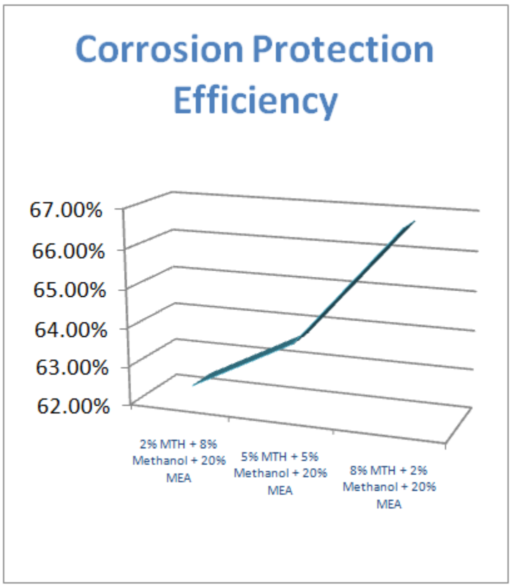

Figure 2: Corrosion Protection Efficiency of different aqueous methionine solutions

Figure 2 displays that as the concentration of methionine is increased in the aqueous methionine solutions, the protection efficiency of the solution also soars with it. For a lower concentration of aqueous methionine solution which is 2% MTH, 8% Methanol, and 20% MEA, the protection efficiency is about 62.40%. For a medium concentration of aqueous methionine solution which is 5% MTH, 5% Methanol, and 20% MEA, the protection efficiency is about 63.77%. For a higher concentration of aqueous methionine solution which is 8% MTH, 2% Methanol, and 20% MEA, the protection efficiency is about 66.81%.

IV. CONCLUSION

The carbon steel corrosion behavior was studied in aqueous methionine solutions at different concentrations of methionine using the weight loss method. It was concluded that methionine has a great inhibition effect on carbon steel corrosion in aqueous methionine solutions. If the concentration of methionine is increased in aqueous methionine solutions, the inhibition efficiency of corrosion will also increase. Moreover, if the concentration of methionine is increased in aqueous methionine solutions, the protection efficiency will also increase. Proving that the inhibition efficiency depends on the concentration and if the temperature was raised while experimenting then it would have depended on it too. As per our experiments, the aqueous methionine solution (8% MTH, 2% Methanol, 20% MEA) gave the best corrosion efficiency of about 0.76 mm/year with a protection efficiency of about 66.81%. The presence of methionine lowers the corrosion rate even much better than other amino acids. In a nutshell, methionine can work as an efficient corrosion inhibitor on a carbon steel surface.

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