Effect of Dimer Acid on The Performance of Morpholine Mono-Amine Base Corrosion Inhibitor

Rafaa M. Esmaael and Maftah H. Alkathafi

Abstract— The effect of dimer acid on the inhibition of morpholine-mono-amine base corrosion inhibitor efficiency has been investigated using different formation of water. The corrosion environment was 100% Sharara field water saturated with CO_2, the addition of dimer acid is to enhance the corrosion inhibitor performance by the action of film persistency on the metal surface. The efficiency evaluation was performed by the comparison of the efficiency with and without addition of dimer acid. A linear polarization technique was applied to obtain corrosion rate and the results have demonstrated that 4% of the efficiency of the chemical inhibitor was improved by adding 1% of the dimer acid.

keywords— Morpholine, Dimer acid, LPR, Formation Water.

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1. INTRODUCTION

The enormous quantities of steel and other metals used in the petroleum industry are prone to corrosion to a more marked degree than in other industrial environments. The severity of the problem is such that about 1 kg of steel and other alloys per ton of oil processed is destroyed due to corrosion. Thus, it is clear that corrosion losses in the petroleum industry are considerable, and it is necessary to adopt corrosion mitigation strategies. One of the most prudent and economic methods of combating corrosion in the oil industry is the use of corrosion inhibitors[1]. Corrosion inhibitor can be defined as a chemical substance or compound when added in small concentration to an environment, effectively, diminishes or controls and prevents the reaction of the metal with the environment. Corrosion inhibitors are added to many systems including: oil and gas production facilities, cooling systems, and refinery systems to reduce the internal corrosion with great efficiency and the key solution to extend the lifetime of those systems. Thus, inhibitors are considered as the first line of defense against corrosion in the oil and chemical industries[2,3]. The inhibitor efficiency depends on its ability to occupy the respective vacant sites forming a chemisorbed inhibitor film. Furthermore, it depends on the composition of the metal, corrodent, inhibitor structure, concentration, and temperature.

1.1 Inhibitors Classification

Corrosion inhibitors can be classified based on their chemical nature or action as:
- Organic or nonorganic.
- Anodic or cathodic.
- Oxidants or not oxidants.

In general, inorganic inhibitors have either cathodic or anodic actions, the organic inhibitors have both anodic and cathodic actions and known as mixed inhibitors, and these inhibitors generally work by an adsorption mechanism. The classification of organic inhibitors depends primarily on its reaction with the metal surface and how the potential on the metal surface is affected. These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal. The inhibitor molecule chemical structureplays a significant role in the inhibition efficiency [4,5]. The effectiveness of organic inhibitor is determined in many ways and its controlled by many factors including:

- The size of the organic molecule.
- The aromaticity and/or conjugated bonding, as the carbon chain length.
- nature and the charges of the metal surface of adsorption mode like bonding strength to metal substrate;
- The type and number of bonding atoms or groups in the molecule (π or σ).
- Capability to form a complex with the atom as a solid within the metal lattice.
- The ability for layer to become compact or cross link [6].

One of the important characteristics of organic corrosion inhibitors, it has to be effectively soluble. The most dominant organic corrosion inhibition mechanism is by adsorbing the organic molecule into the metal-solution interface. However, the modes of adsorption are dependent on the following:

- ❑ The chemical structure of molecule.
- ❑ The chemical composition of the solution.
- ❑ The nature of the metal surface.

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□ The electrochemical potential at the metal-solution interface.

There are three principal types of adsorption associated with organic inhibitors:

- π -bond orbital adsorption
- Electrostatic adsorption
- Chemisorption.

In general, it appears likely that the most effective organic inhibitor is one whose electron density distribution causes the inhibitor to be attracted to both anodic and cathodic areas[7].

1.2 Corrosion Inhibition Measurements

There are different techniques to measure the inhibition efficiency of corrosion inhibitor including, Visual, Weight loss specimens, Electrical resistance probes and Linear polarization resistance.

1.2.1 Linear Polarization Resistance

Linear polarization resistance (LPR) technique is commonly used for measuring corrosion rates for both laboratory and field corrosion studies. This technique is based on the mixed potential theory, the slope of the polarization curve measured near the mixed or corrosion potential E_{corr} of a corroding electrode is inversely proportional to the reaction rate of the electrode. The net current density (i_{net}), which circulate through a metal-electrode of corroding electrode interface, is given by the expression:

$$i_{net} = i_a - i_c$$

Where:

i_a - is the anodic current density
i_c - is cathodic current density, and
i_{net} - is the net current density across the
        metal-electrode interface.

$$i_a = i_o \exp [\, E - E_o/ \beta_a \,]$$

$$i_c = i_o \exp [\, E - E_o/ \beta_c \,]$$

The overall expression of the form is:

$$I_{net} = i_{corr} [\, \exp (\eta / \beta_a) - \exp (\eta / \beta_c) \,$$

where: η - is the over potential.
       β - is the reaction's Tafel constant

The last equation shows that the net current density exponentially depends on the over potential η and assuming that:

- The determining step in the electrochemical corrosion reaction is the charge transfer at the metal-electrolyte interface, (activation control mechanism).
- Solution resistance and surface film can be neglected.
- Concentration polarization is absent.
- There is no secondary electrode reaction occurring.

Based on the assumptions above, the final corrosion current density equation becomes:

$$I_{corr} = b_a \, b_c \, /2.303 \, (\, b_a + b_c \,) \, (\delta_i / \delta_E \,) = B/R_p$$

If B is known, then the corrosion current density can be measured. It can be obtained in several ways including; considering theoretical Tafel slopes, obtaining the value of Tafel separate polarization experiments in identical conditions, taken value from literature for similar corrosion systems or by calibration of the B constant using weight loss measurements. To measure R_p (polarization resistance), the electrode should be polarized in both the cathodic and anodic directions, close to the corrosion potential. The electrode usually polarized to ± 20mv from its open circuit corrosion potential (E_{corr}) [8,9].

2. EXPERIMENTAL METHOD

2.1 Corrosion Measuring Technique

ACM Gill-12 linear polarization technique is employed for this work. This device contains 12 glass corrosion measuring cells placed in a water bath to control the temperature inside the cells, each cell has two LPR steel electrodes, all cells are connected to the computerized potentiostatic panel. The software gives the ability to switch between cells and read from each cell at the same time. Each cell is connected to CO_2 gas bubbling system through a rubber tube carrying the gas from a gas regulator system, Figure.1 shows the components of Gill-12 technique.

Fig. 1. The components of Gill-12 technique.

2.2 Formation Water Samples

Three formation water samples were collected from different oil production wells in the sharara oil field. pH, CO_2, temperature and alkalinity were tested at W6,W12, and A20 well heads. The analysis of water was done at the Jowfe oil technology laboratories in Benghazi city. Table 1 shows the collected water samples analysis.

Table 1. Formation water analysis

Ion (mg/l)	W6	W12	A20

pH	6.8	6.7	6.5
Na^+	1021	2584	1726
Ca^{+2}	20	386	252
Mg^{+2}	8	159	92
Ba^{+2}	0.6	0.3	0.2
Sr^{+2}	0.3	10	5
Fe^{+2}	1	4	1
Cl^-	1070	5051	4117
HCO_3^-	790	310	310
SO_4^{-2}	158	465	448
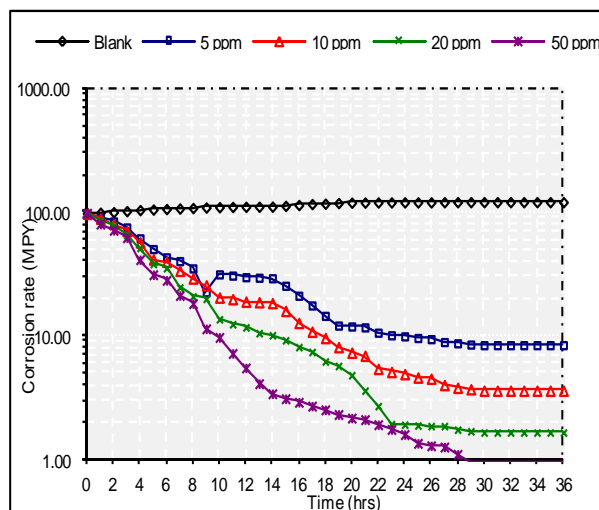
Fig. 2. Corrosion rate vs time for R1 in W6 formation water

Fig. 3.Corrosion rate vs time for R2 in W6 formation water

2.3 Experiment Test Condition

To ensure the optimum LPR results that reflect the operation condition at the oil filed the LPR corrosion cells were bubbled with CO_2 for 1 hr to make sure that the water samples were saturated with CO_2 gas before running the test. The test was conducted at 70 C^0 which slightly above the operation temperature at the oil field. The LPR electrode material was 1018 low carbon steel.

2.4 Corrosion Inhibitors

Morpholine is an organic chemical compound having the chemical formula of $O(CH_2CH_2)_2NH$. There are two types of water soluble filming amine corrosion inhibitors were used in this study named R1 and R2. R1 has the active material as a Morpholine mono-amine with addition of 1% dimer acid ($C_{36}H_{68}O_4$) to enhance the adhesion of filming amine on the metal surface. R2 is just a morpholine mono-amine without dimer acid. Different inhibitor concentrations have been used in this study, 5 ppm, 10 ppm, 20 ppm, and 50 ppm inhibitor and blank sample with no inhibitor.
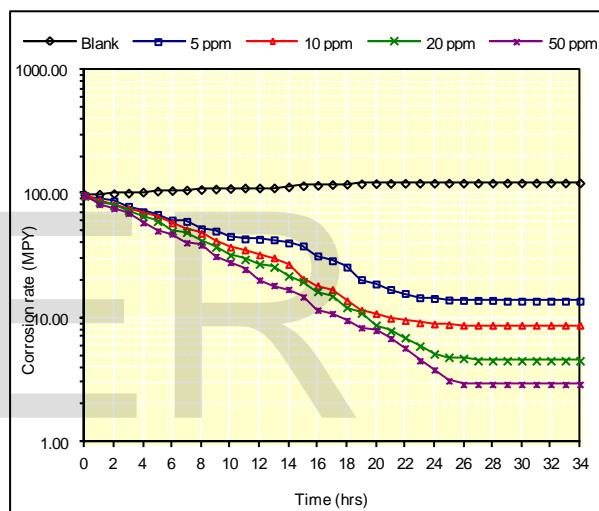
3. RESULTS AND DISCUSSIONS

Figure 2 shows the corrosion rate as a function of time in hours at different R1 concentrations ranged from 0-50 ppm. As can be seen, when the concentration of inhibitor increases the rate of corrosion decreasing compared with the blank sample. Similar behavior with lower inhibition efficiency was observed for R2 which have no dimer acid added as illustrated in Figure 3. Figure 4, shows the inhibition efficiency of R1 and R2 in the same corrosion environment using W6 formation water. It is clearly that the inhibitor containing dimer acid (R1) exhibit better efficiency than (R2) which is without dimer acid. Figures 5-10 represent the same behavior at different formation water, these results indicated improvement in the performance of inhibitor with the addition of dimer acid.
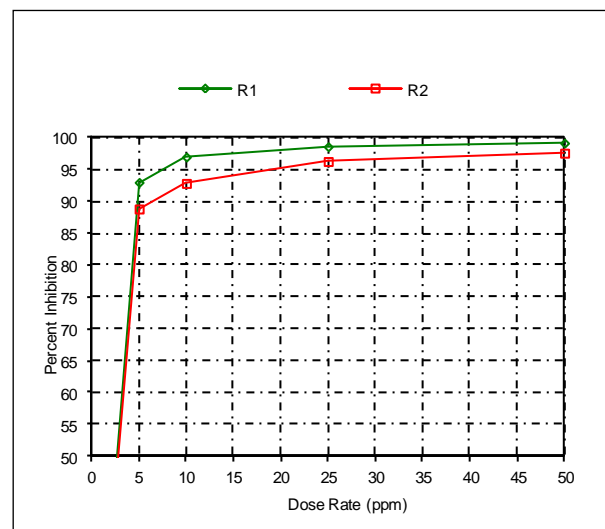

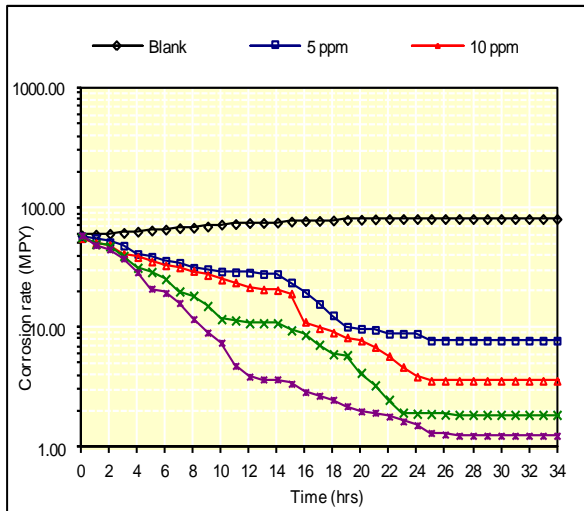Fig. 4. W6 dose rate vs percent inhibition

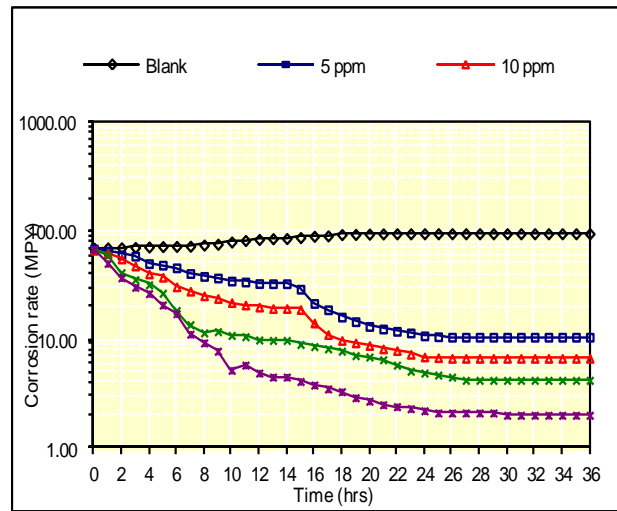Fig. 5. Corrosion rate vs time for R1 in W12 formation water

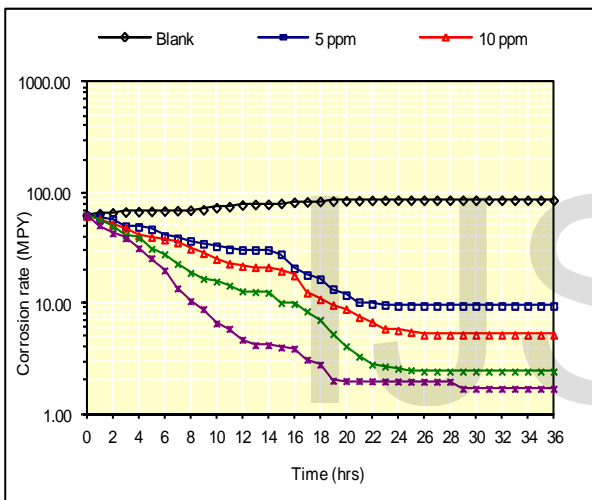Fig. 8.Corrosion rate vs time for R1 in A20 formation water

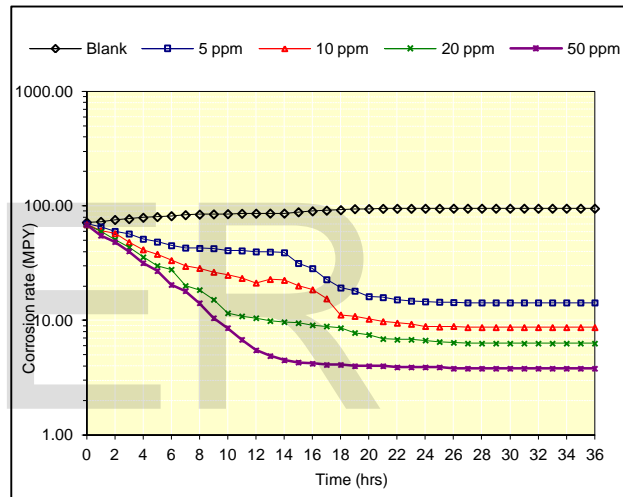Fig. 6.Corrosion rate vs time for R2 in W12 formation water

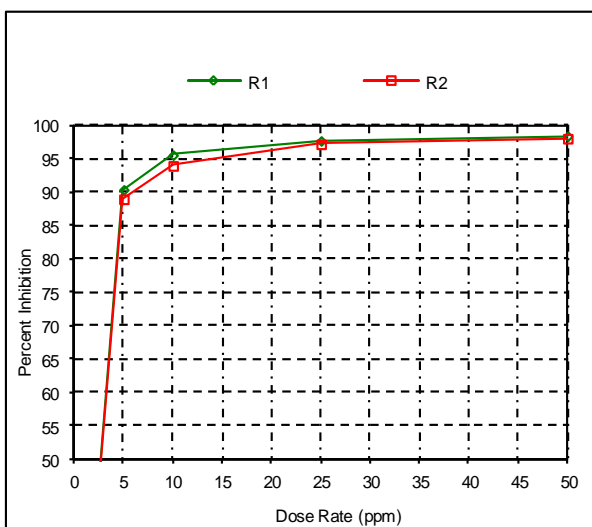Fig. 9.Corrosion rate vs time for R2 in A20 formation water
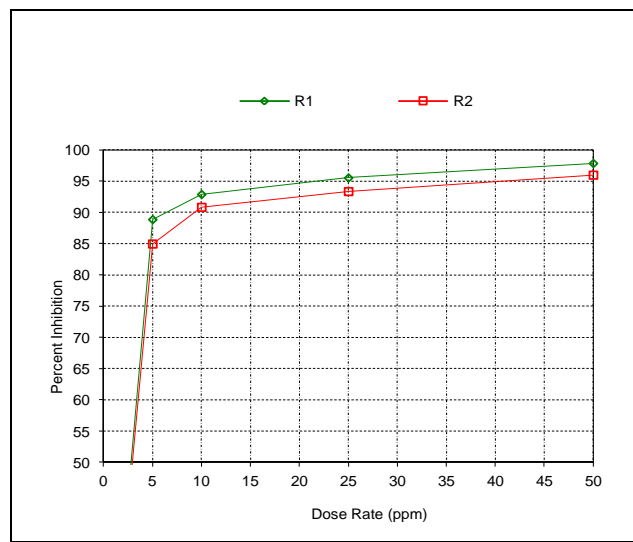

Fig. 7. W12 dose rate vs percent inhibition

Fig. 10. A20 dose rate vs percent inhibition

4. CONCLUSIONS

Based on the results obtained from the laboratory study, it can be concluded that dimer acid has a positive effect on the inhibition efficiency when added to morpholine base inhibitor. It enhance the film persistency and the film adhesion on the metal surface. The inhibitor efficiency is improved about 4% compared with the inhibitor free of dimer acid.

5. REFERENCES

[1]. Mark E. Orazem, Underground pipeline corrosion, Detection, analysis and prevention, Woodhead Publish ing Limited, UK, 2014.

[2]. Dariva, C.G.; Galio, A.F. Corrosion inhibitors- princi ples, mechanisms and applications. In Developments in Corrosion Protection; Aliofkhazraei, M., Ed.; INTECH: Winchester,UK, 2014; pp. 365–379.

[3]. C.CNathan,Corrosioninhibitors,National Association of Corrosion Engineers, Houston,Texas,1994.

[4]. M. S. Al-Otaibi, A. M. Al-Mayouf,. M. Khan, A. A. Mousa,S. A. Al-Mazroae H. Z. Alkhathlan, corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, Arabian Journal of Chemistry, 2012,pp. 1-7.

[5]. I.B.Obot,N.O.Obi-Egbedi,S.A.Umoren, Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl, Journal of Corrosion Science, vol. 51, issue 8, 2009, pp. 1868-1875.

[6]. A. Yıldırım, M. Çetin, Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors, Journal of Corrosion Science, vol. 50, 2008, pp.155-165,.

[7]. V. Gentil, Corrosão, 2003, 4th ed., Rio de Janeiro:LTC.

[8]. Fontana M. G.; Staehle; R.W., Advancesin Corrosion Science and Technology, Volume 6,Plenum Press, USA,2013.

[9]. American Society for Testing and Materials, G-102-189, ASTM, USA,1991,.