

Protecting Oil Flowlines from Corrosion Using 5-ACETYL-2-ANILINO-4-DIMETHYLAMINOTHIAZOLE

FATIMA MAHMOOD SHAKER¹, DHIFAF JAAFAR SADEQB²¹Basra Oil Company, Rumaila oil Filed, Iraq, fatima.shaker2008m@coeng.uobaghdad.edu.iq²Department of Petroleum Engineering, University of Baghdad, Baghdad,

Correspondence to: Dhifaf Jaafar Sadeqb, Email: Iraq,Dhifaf.Sadeq@coeng.uobaghdad.edu.iq

ABSTRACT

Oil flow lines are used to transport oil and its derivatives from a well over long distances, and because oil wells produce other potentially corrosive products, such as carbon dioxide and Hydrogen sulfide, it is necessary to take methods to protect the pipeline from corrosion. One of these methods is the use of corrosion inhibitors in this study. Prepare 5-acetyl-2-anilino-4-dimethylaminothiazole and test it as a corrosion inhibitor on a sample of the Rumaila flow line at a constant temperature 25°C in (3.5%) NaCl and (3.5%) KCl solution in the absence and presence of different concentrations of inhibitor (0 mM, 0.01 mM, 0.03 M, 0.05 mM). by using liner polarization (Tafel slope). The inhibitor exhibited the best performance at high concentration giving 94% in NaCl solution and 88% in KCl solution and solution, the inhibitor gave It was used FT-IR to find out the effective aggregates in the inhibitor, Tafel plot reveals that Ecorr for flowline in the presence the inhibitors shift to a higher (noble) position compared with blank solution, implying that the protection acts as an anodic protection.

Keywords: corrosion inhibitor, oil flowline, leaks.

INTRODUCTION

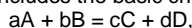
Flowline carry crude oil or its products from one site to another. Oil pipelines are classified into three types based on their intended use. First, collection lines, which have a small diameter and are used to transport crude oil over short distances. Second, transportation pipes, also known as feeders, are larger in diameter than collection pipelines and convey oil from storage or refinery units to distribution pipelines. The third type of pipeline is a transmission pipeline, which has the biggest diameter and is used to carry various grades of crude oil from the production region to the final consumption location [1].

Flowline are sometimes buried underground, with just valves, pumping or compressor stations, or terminals indicating their presence [2]. Corrosion has caused pipeline failures, which are generally expensive to repair, both in terms of lost or tainted goods, environmental harm, and perhaps human safety [3]. Crude oil is a complicated mixture of hydrocarbons that is used to save energy all over the world. Because of their capacity to create highly adherent layers on the metal surface, these liquid hydrocarbons may help to minimize corrosion in many circumstances. Impurities such as H₂S, CO₂, naphthenic acids, and chlorides, on the other hand, can accelerate the corrosion of steel pipelines and equipment used in the exploration, production, transportation, and refining of petroleum [4].

Every year, the major oil companies lose billions of dollars due to corrosion, and they must cover the cost of maintenance management. The cost of corrosion in the oil and gas industry is projected to be US\$1.372 billion yearly. Corrosion is a major threat to the integrity of assets in all component areas, according to the industries. Corrosion causes serious resource degradation in addition to direct losses. The cost of repairing damaged infrastructure is costly, but it may be cut in half if suitable corrosion prevention techniques are being used. At the same time, harmful compounds should be prevented. Protecting one at the expense of the other is not a good option. Extended component life is required to maintain the extensive metallic infrastructure, particularly in distant and hostile areas, so that overall service life is increased and costly maintenance is reduced. Corrosion management does not always necessitate the establishment of a "zero corrosion rate" system; rather, effective monitoring and inspection procedures are required to ensure acceptable corrosion rates, allowing the system to operate reliably and safely [5].

Corrosion is the result of a material's interaction with its surroundings [6]. Corrosion is the breakdown of a metal due to an electrochemical interaction with its environment [7]. Corrosion is usually caused by a series of redox reactions that are electrochemical in nature. At anodic sites, the metal is oxidized to corrosion products, whereas at cathodic sites, some species are

reduced [8]. Corrosion, on the other hand, has been characterized as "unwanted degradation" of a metal or alloy, i.e., an interaction of the metal with its environment that negatively affects the metal's qualities that must be retained [9]. Finally, corrosion is an irreversible interfacial interaction between a material and its environment that results in material loss due to the dissolution of one of the environment's elements into the substance [10]. Corrosion may alternatively be thought of as a heterogeneous chemical reaction that takes place at metal/nonmetal interfaces and includes the basic chemical equation:



where A represents the metal and B represents the nonmetal reactions, and C and D represent the reaction products [11].

Corrosive conditions abound in the petroleum industry. Some of these are specific to the industry. As a result, it is practical to combine all of these environments together. In the petroleum business, corrosion issues arise in at least three areas: (1) production, (2) transportation and storage, and (3) refinery operations [12]. Sweet corrosion, sour corrosion, and microbiologically influence corrosion (MIC), which cause pitting corrosion on the steel pipeline surface are the most common problems connected with pipelines used in the transportation of oil and gas. Sweet corrosion is caused by the presence of carbon dioxide and water, with the carbon dioxide dissolving in the water to form carbonic acid, which reacts with the steel pipeline to cause corrosion damage. Sour corrosion is caused by the presence of water and hydrogen sulphide in the pipeline, while MIC occurs when sulphate-reducing bacteria produce by-products from the organisms, which promote several forms of corrosion [13].

Improvements in the material of construction, application of protective coatings, cathodic protection, and application of inhibitors to change the corrosive environment have all been used to prevent and control corrosion of oil and gas pipelines [14]. Inhibitors are among the most widely used methods of corrosion treatment and are categorized as inorganic, organic, surfactant, or mixed substance inhibitors. Surfactants, also known as surface active agents, are molecules with a polar hydrophilic head and a non-polar hydrophobic tail. Depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface, the inhibitory action of surfactant molecules in aqueous solution could be due to physical (electrostatic) adsorption or chemisorptions onto the metallic surface. Corrosion of materials occurs when oxygen and moisture are present, and it includes two electrochemical reactions: oxidation at the anodic site and reduction at the cathodic site [15].

The organic compounds have numerous bonds in their structures, which mostly comprise nitrogen, Sulphur, and oxygen

atoms, and are adsorbed on metal surfaces [16]. Heterocyclic compounds with polar functional groups and conjugated π -electrons of double and triple bonds are the most often utilized corrosion inhibitors because they act as adsorption sites during metal-inhibitor interactions. Through their adsorption sites, these inhibitor compounds adsorb on metal surfaces and protect against corrosion [17]. Corrosion inhibitors work by forming a protective film on the metal preventing corrosive elements contacting the metal surfaces, as illustrated in Figure (1) [18]. Adsorption of organic inhibitors depend on inhibitor's molecular structure, the existence of active surfaces in their structure, the charge of the metal employed, and the kind of corrosive electrolytes [19].

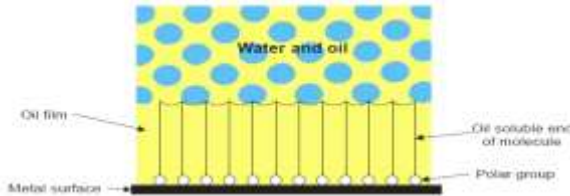


Figure 1: Simple schematic showing how inhibitor film prevents water contacting a metal surface.

METHODS

Synthesis of thiazole: Thiazole was synthesized commercially Figure (2) shows the product.



Figure 2: shows the product(5-Acetyl-2-anilino-4-dimethylaminothiazole)

Carbon steel preparation (sample of flowline): The flowline specimens used in the experiment were immersed in an HCl acid (1.0 M) solution for one minute. Figure (3) depicts an example of a flow line. After the flooding step, the carbon steel specimen was thoroughly cleaned with distilled water and dried using towels. The surface of the carbon steel specimen was cleaned with sand paper of various grades and sizes, including 800, 1000, 1200, and 1500. The carbon steel specimen was washed with distilled water and then soaked in alcohol to remove the grease. The techniques outlined above were used to obtain carbon steel for the experiment, to fit the experiment, cut it into discs The carbon steel is depicted in Figure(3) &(4), the chemical composition of flow line shows in table (1)

Table 1: Chemical composition of carbon steel.

metal	C%	Si%	Mn%	S%	P%	v%	Nb%	Ti%	other%
Carbon Steel 45	0.18	0.45	1.70	0.015	0.025	g	g	g	h,i

g unless otherwise agreed, Nb +V + Ti \leq 0.15%
 h unless otherwise agreed, Cu \leq 0.50%, Ni \leq 0.50%, Cr \leq 0.50% and Mo \leq 0.15%
 i h unless otherwise agreed, Cu \leq 0.50%, Ni 1.00 %, Cr \leq 0.50 % and Mo \leq 0.15%



Figure 3: the sample of pipe.

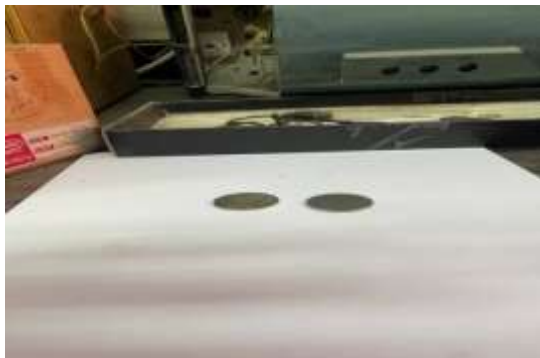


Figure 4: the sample of pipe after cutting.

Equipment and apparatus (liner Polarization Technique): The corrosion cell is made from pyrex, has a capacity of 1 liter, includes inner and outer containers, and has 3 electrodes The three poles may be interpreted as:

- A A reference electrode become used to decide the voltage of the operating electrode in step with the potential of the reference electrode. The potential of the reference electrode is thought and precise. It is blended from tubes. The inner tube carries AgCl, Ag, KCl, the reference electrode stands at a distance of 2 mm from the working electrode.
- B The auxiliary electrode is made from excessive purity platinum metallic; It is 10 cm long.
- C The working electrode is the subject under study, since its potential have to be measured.

This electrode become formed from a metallic wire of 20 cm in length and linked to the composite specimen. The tested sample become inserted into a corrosion cell and the diameter of the floor exposed to the solution was (16.55 cm²). Figure (5) shows the complete system set up of polarization measurement.

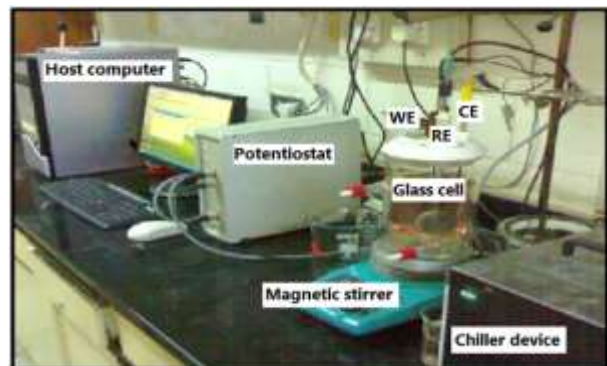


Figure 5: Photograph of complete system set up for polarization measurements.

Experimental Procedure of polarization measurement: The experimental procedure which was followed in this study involved: Samples were cleaned by washing with distilled water, dried and stored in a desiccator until used, One liter of NaCl or KCl solution was prepared at (3.5%) concentration with distilled water, and the solution was transferred to a clean corrosion cell

The specimen of flowline was mounted on the working electrode holder. The auxiliary electrode, (silver -silver chloride) electrode and other components were put into the corrosion cell. The (RE) (silver-silver chloride) was placed as close as possible to the surface of the (WE), and then the electrode was filled with the test solution. The electrochemical cell must be connected to the device by a suitable cable. The potentiostat and computer were turned on in order to start the measurements. the operating system involves sending a set of commands from the computer to the potentiostat.

The open circuit voltage is the initial programmed step in this test, and the polarization curve will begin at the open circuit voltage over a potential range about ± 200 millivolts from open circuit. The Corrosion current density (i_{corr}) and corrosion potential (E_{corr}), were determined from the polarization curve. The work was carried out at a temperature of 25°C Corrosion inhibitors were added with different concentrations and differen, and the inhibition efficiency was calculated in each step.

Characterization of (5-Acetyl-2-anilino-4-dimethylaminothiazole): The function group of the compound were determined by FT-IR.

RESULTS AND DISCUSSION

The formation of thiazole was proven via FT-IR results, indicating CH₃, CH-str. at 2831.31 cm⁻¹; (c) The length of C-N is 1413.72 cm⁻¹; C=O stretching at 1691.46 cm⁻¹; C=N stretching at 1639.38 cm⁻¹; C-S stretching at 692.40cm⁻¹; C=C stretching at 1564.16 cm⁻¹; N-H stretching at 3282.62 cm⁻¹.

Figure (6) shows the structure of the thiazole, Figure (7) shows the FT-IR spectrum of thiazole. Table (2) shoes the spectral analysis of thiazole.

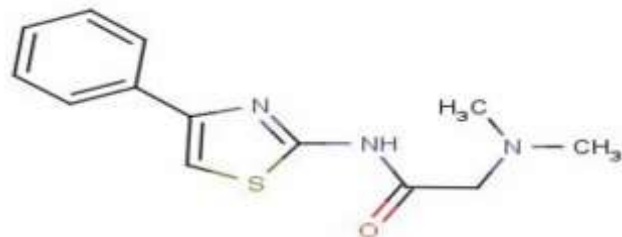


Figure 6: Structure of thiazole

Table 3: Corrosion data of carbon steel in (3.5%) NaCl at absence and presence different concentration of inhibitor at temperature 25°C.

inhibiter	E corr.	I corr.	I corr./ r	Resis.	Anodic β	Cathodic β	Corr. rate,	IE%
Blank	-0.998	146.4	1.464E-4	523.8	0.950	0.217	0.718	-
0.01	-0.698	21.04	2.104E-5	1793	0.160	0.190	0.103	86
0.03	-0.682	15.03	1.503E-5	2207	0.117	0.220	0.074	90
0.05	-0.707	8.159	8.159E-6	3667	0.115	0.173	0.040	94

Table 4: Corrosion data of carbon steel in (3.5%) KCl at absence and presence varies concentration of inhibitor at temperature 25°C.

inhibiter	E corr.	I corr.	I corr./ r	Resis.	Anodic β	Cathodic β	Corr. rate,	IE%
Blank	-0.978	155.0	1.550E-4	500.5	1.183	0.210	0.761	-
0.01	-0.709	22.74	2.274E-5	1970	0.166	0.273	0.112	85
0.03	-0.677	20.29	2.029E-5	1477	0.105	0.201	0.100	87
0.05	-0.723	18.57	1.857E-5	2415	0.182	0.238	0.091	88

Figures (8) and (9) shows (Tafel plot) the potentiostatic polarization curves (potential vs current density) for flowline corrosion in (3.5%) NaCl and (3.5%) KCl in the absence and presence of different concentrations of inhibitor at temperature 25°C. It was noted in the tables (3) and (1.4)resulting from the

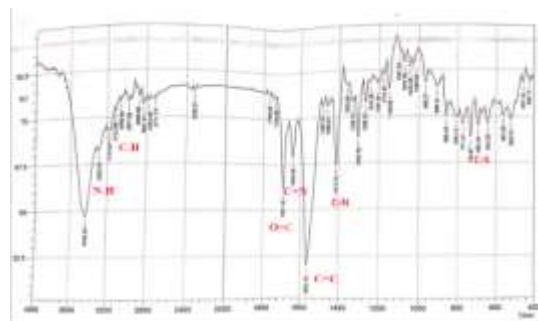


Figure 7: The FT-IR spectrum of thiazole

Table 2: Spectral analysis of thiazole

Compound	FT-IR (KBr)
AAD	CH ₃ , CH-str. at 2831.31 cm ⁻¹ C-N stretching at 1413.72 cm ⁻¹ C=O stretching at 1691.46 cm ⁻¹ C=N stretching at 1639.38 cm ⁻¹ C-S stretching at 692.40cm ⁻¹ C=C stretching at 1564.16 cm ⁻¹ N-H stretching at 3282.62 cm ⁻¹

The corrosion parameters were evaluated from the resulting data in Tables (3) and (4) and figures (8) and (9) The corrosion current density (i_{corr}), and corrosion potential (E_{corr}) were obtained by the extrapolation of the cathodic and anodic Tafel. The anodic (ba), cathodic (bc) Tafel slopes were also calculated from figures. tables show the resulting data of the corrosion potential E_{corr} (mV), corrosion current density i_{corr} (A/cm²), cathodic and anodic Tafel slopes bc and ba (mV/Dec), weight loss WL (g/m². d), penetration loss PL (mm/y), and protection efficiency PE% which are calculated from equation (1.1).

The inhibition efficiency (%IE) was calculated by the following equation

$$\%IE = \frac{(i_{corr}o - i_{corr})}{(i_{corr}o)} \times 100 \quad 1.1$$

Where ($i_{corr}o$) is the corrosion current density in the absence of inhibitor, and (i_{corr}) is the corrosion current density in the presence of inhibitors[20-23] .

calculations that increasing the concentration of the inhibitor material increases the efficiency of corrosion inhibition as the corrosion current decreases and the corrosion rate decreases, Tafel plot reveals that E_{corr} for flowline in the presence the inhibitors shift to a higher (noble) position compared with blank

solution, implying that the protection acts as an anodic protection.

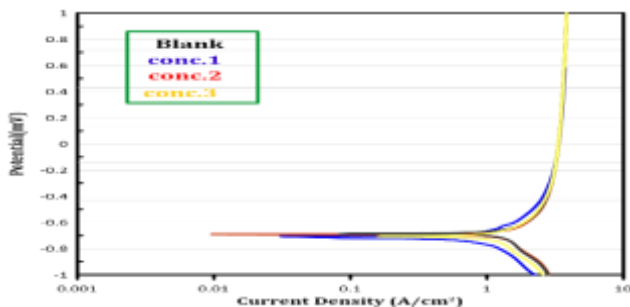


Figure 8: Polarization plots of carbon steel in (3.5%) NaCl for various concentrations of inhibitor at temperature 25°C.

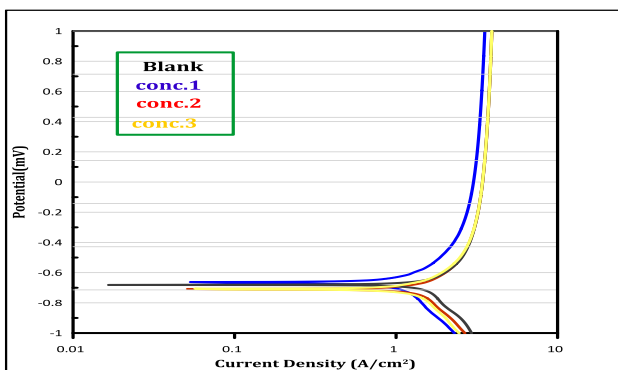


Figure 9: Polarization plots of carbon steel in (3.5%) KCl for various concentrations of inhibitor at temperature 25°C.

CONCLUSION

Electrochemistry has proven its strength in studying the corrosion resistance of carbon steel. The experiments performed in this scientific project were to use Tafel Curve and to test the efficacy of thiazoles as corrosion inhibitors on a sample in saline solution the results showed that the corrosion resistance of thiazoles as corrosion inhibitors is able to reduce and delay the corrosion technique on the flowline. For experiments with different concentrations at the same temperature, 25°C, the effects confirmed that the best effective inhibitor was 0.05 mM, with 94% for NaCl solution ,88% for KCl solution, Increasing the concentrations of corrosion inhibitors will result in lower current and lower corrosion rate. In the end, the study achieved the desired goal.

Funding: The study did not receive any specific funding.

Conflict of Interests: None

REFERENCES

- Jasim HH. Evaluation the effect of velocity and temperature on the corrosion rate of crude oil pipeline in the presence of CO₂/H₂S dissolved gases. *Iraqi Journal of Chemical and Petroleum Engineering*. 2019 Jun 30;20(2):41-50.
- Murrill BJ. Modes of Constitutional Interpretation. InCRS Report for

- Congress 2018 Mar 15 (Vol. 45129).
- Kolawole FO, Kolawole SK, Agunsoye JO, Adebisi JA, Bello SA, Hassan SB. Mitigation of corrosion problems in API 5L steel pipeline-a review. *Journal of Materials and Environmental Sciences*. 2018;9(8):2397-410.
- Dedhk C., Miekerey N., Silveira H.P, Sardari O. (2002) crude oil Analysis. *Spectrochim. Acta B* 57979- 990.
- Khalifa T. Corrosion problems and solutions in oil gas refining and petrochemical industry201910... *Koroze a ochrana materiálu*. 2017;61(3):100-17.
- H.H. Uhlig, "The Corrosion Hand book". 1948, Wiley (New York) and Chapman and Hill, London.
- AlMashhadani HA, Saleh KA. Electro-polymerization of poly Eugenol on Ti and Ti alloy dental implant treatment by micro arc oxidation using as Anti-corrosion and Anti-microbial. *Res. J. Pharm. Technol*. 2020 Oct 1;13(10):4687.
- Fontana MG, Greene ND. *Corrosion Engineering*.
- Lyon S. *Corrosion for Science and Engineering*. *Corrosion Science*. 1996;8(38):1425-6.
- R.H. Perry and D.W. Green, "Chemical Engineers", Handbook, 1997, 7th ed., Australia, pp.28-38.
- Landolt D. *Corrosion and surface chemistry of metals*. EPFL press; 2007 May 2.
- Gilbert PT, Shreir LL, Jarman RA, Burstein GT. *Corrosion: Metal/Environment Reaction*.
- Prabh.S.S, Rathish. R.J., R.Dorothy, Brindha.G., M.Pandiarajan, Al-Hashem.A., and, Rajendran.S., "Corrosion Problems in Petroleum Industry and their Solution", *Eur.Chem.Bull*, 3(3), pp 300-307, 2014 .
- Al-Mashhadani HA, Alshujery MK, Khazaal FA, Salman AM, Kadhim MM, Abbas ZM, Farag SK, Hussien HF. Anti-Corrosive Substance as Green Inhibitor for Carbon Steel in Saline and Acidic Media. In *Journal of Physics: Conference Series* 2021 Mar 1 (Vol. 1818, No. 1, p. 012128). IOP Publishing.
- Popoola LT, Grema AS, Latinwo GK, Gutti B, Balogun AS. Corrosion problems during oil and gas production and its mitigation. *International Journal of Industrial Chemistry*. 2013 Dec;4(1):1-5.
- Kolawole FO, Kolawole SK, Agunsoye JO, Adebisi JA, Bello SA, Hassan SB. Mitigation of corrosion problems in API 5L steel pipeline-a review. *Journal of Materials and Environmental Sciences*. 2018;9(8):2397-410.
- A.Kumar, *E-Journal of Chemistry*, 5 (2008) 275 .
- Kadhim MM, AlMashhadani HA, Hashim RD, Khadom AA, Salih KA, Salman AW. Effect of Sr/Mg co-substitution on corrosion resistance properties of hydroxyapatite coated on Ti-6Al-4V dental alloys. *Journal of Physics and Chemistry of Solids*. 2022 Feb 1;161:110450.
- Raj XJ, Rajendran N. Corrosion inhibition effect of substituted thiadiazoles on brass. *International Journal of Electrochemical Science*. 2011 Feb 1;6(2):348-66.
- J. Hobbs, "Reliable corrosion inhibition in the oil and gas industry HSE Books Health and Safety Executive," *Heal. Saf. Exec.*; pp. 1-27, 2014, [Online]. Available: www.nationalarchives.gov.uk/doc/open-government-licence/
- El-Hajjaji F, Messali M, Aljuhani A, Aouad MR, Hammouti B, Belghiti ME, Chauhan DS, Quraishi MA. Pyridazinium-based ionic liquids as novel and green corrosion inhibitors of carbon steel in acid medium: electrochemical and molecular dynamics simulation studies. *Journal of Molecular Liquids*. 2018 Jan 1;249:997-1008.
- Abdallah M. Corrosion behaviour of 304 stainless steel in sulphuric acid solutions and its inhibition by some substituted pyrazolones. *Materials Chemistry and Physics*. 2003 Dec 20;82(3):786-92.
- F. Bentiss, M. Lagrenee, M. Traisnel, The corrosion inhibition of mild steel in acidic media by a new triazole derivative, *J.C. Hornez, Corros. Sci.*, 1999, 41(4), pp.789-803.